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**PREPARATION AND CHARACTERIZATION OF CATION EXCHANGE
RESINS BASED ON LOCALLY-FABRICATED POLYETHYLENE
PALLETS**

PROF. DR. MOHAMED MAHMOUD EL-SAYED NASEF

**PUSAT PENGURUSAN PENYELIDIKAN
UNIVERSITI TEKNOLOGI MALAYSIA**

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DEDICATION

‘To those who strongly believe that today’s dreams are tomorrow’s facts’

ABSTRACT

The objective of the present project was to prepare and characterize cation exchange resins based locally fabricated low density polyethylene (LDPE) using radiation induced grafting method. The resins denoted as LDPE-g-PSSA were prepared by radiation induced grafting of styrene monomer onto LDPE particles followed by sulfonation reaction to introduce sulfonic acid moiety. The effect of various reaction parameters such as monomer concentration, irradiation dose, diluting solvent addition of inhibitor and addition of acid on the degree of grafting of the resins were investigated. The degree of grafting was found be heavily dependent upon the investigated parameters in a way that led to a close control over the composition of the resins. The introduction of polystyrene to LDPE resins and subsequent sulfonation was confirmed by FTIR spectral analysis. The water uptake and the ion exchange capacity of the obtained resins were evaluated. The thermal properties, thermal stability and mechanical stability of the obtained cation exchange resins were also studied using differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), respectively. X-ray diffraction was also used to determine the structural changes took place in LDPE in correlation with the two-step procedure i.e. grafting and sulfonation and variation of the degree of grafting. The physical and chemical properties of the obtained resins we found to be strongly dependent on the degree of grafting. The obtained resins were found to have very good combination of properties compared to corresponding commercial sulfonated resins. It can be concluded that radiation grafted LDPE-g-PSSA resins have potential to be applied in water and waste water treatment. Moreover, radiation induced grafting is a convenient method to cation exchange resins.

ABSTRAK

Objektif projek ini adalah untuk menyediakan dan mencirikan resin penukaran ion menggunakan polietilena berketumpatan rendah (LDPE) tempatan melalui pencantuman teraruh sinaran. Resin dikenali sebagai LDPE-g-PSSA telah disediakan melalui pencantuman teraruh sinaran terhadap monomer stirena ke atas zarah LDPE dan diikuti dengan tindakbalas pensulfonan untuk memperkenalkan asid sulfonik. Kesan terhadap pelbagai keadaan pencantuman seperti kepekatan monomer, dos penyinaran, pencairan pelarut terhadap penambahan bahan kimia penghalang serta penambahan asid kepada darjah pencantuman adalah dikaji. Darjah pencantuman didapati sangat bergantung kepada keadaan yang telah dikaji, yang menjurus kepada pengawalan ketat terhadap komposisi resin-resin tersebut. Pengenalan polistirena ke atas resin-resin LDPE diikuti dengan pensulfonan telah disahkan oleh analisis spektrum FTIR. Kadar pengambilan air dan kapasiti penukaran ion juga telah diselidiki. Sifat haba, kestabilan haba dan kestabilan mekanik terhadap resin penukaran kation telah dikaji menggunakan *differential scanning calorimetry* (DSC), *thermal gravimetric analysis* (TGA). *X-ray diffraction* juga telah digunakan untuk menentukan perubahan struktur yang berlaku di dalam LDPE berkadaran dengan kaedah dua-langkah iaitu pencantuman dan pensulfonan serta variasi darjah pencantuman. Sifat fizik dan kimia resin yang diperolehi didapati sangat bergantung kepada darjah pencantuman. Resin yang diperolehi didapati mempunyai kombinasi sifat yang sangat baik berbanding dengan resin pensulfonan komersial. Kesimpulannya resin pencantuman sinaran LDPE-g-PSSA mempunyai potensi untuk diaplikasi di dalam perawatan air dan air sisa. Tambahan pula, sinaran pencantuman teraruh adalah kaedah mudah untuk menghasilkan resin penukaran kation.

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LIST OF SYMBOLS

W_g	Weight of grafted resin (g)
W_o	Weight of original resin (g)
W_w	Weight of wet resin (g)
W_d	Weight of dry resin (g)
ΔH_m	Heat of Melting PE resins (J/g)
ΔH_{m100}	Heat of Melting 100% crystalline PE resins (J/g)
m_{PE}	Weight fraction of PE
m_{PS}	Weight fraction of PS
m_{pssA}	Weight fraction of sulfonated polystyrene grafts
T_g	Glass transision temperature (°C)
T_m	Melting temperature (°C)

LIST OF ABBREVIATION

PE	Polyethylene
LDPE	Low density polyethylene
PE-g-PS	Polyethylene grafted with styrene
PE-g-PSSA	Sulfonated polyethylene grafted with styrene
FTIR	Fuorier transform infra red
ATR	Attenuated total Reflectance
IEC	Ion exchange capacity
XRD	X-ray diffractometry
DSC	Differential scanning calorimetry
TGA	Thermal gravimetry analysis

CHAPTER 1

INTRODUCTION

1.1 Background

Ion exchange resins are class of materials that are receiving an increasing attention due to their wide industrial applications in flocculation, separation and purification in various industrial applications including the treatment of radioactive waste of nuclear power plants. The early great success of ion exchange in the area of water purification and water softening prompted extending the use of the technology for various applications including desalination of sea and brackish water, removal of heavy metals from industrial streams, removal of dyes and colors, removal of nitrate and ammonia, removal of fluoride and dealkalization (Zagorondi, 2007).

Ion exchange resins available in two basic categories; anion exchange and cation exchange depending on the type of ionic group attached to the polymer host. The presence of ionic charged groups in the resins confers them a unique property (permselectivity) to selectively inhibit or reject the adsorption of certain ionic species depending on fixed charged group. Negative groups such as SO_3^- and $-\text{COO}^-$ provide cationic exchange properties, whereas positive groups such amines (NH_3^+) provide anionic properties. The permselectivity of these resins is due to the tendency of the ionic charged groups to exclude co-ions (ions of similar charges to the fixed ionic groups) by electrostatic repulsion. The extent of this exclusion is mainly governed by the concentration of the fixed ionic groups (ion exchange capacity).

Ion exchange resins can be prepared by chemical, photochemical, mechanical and radiochemical techniques. The approaches to introduce ion exchange groups into the resin substrates can be classified into three categories based on the starting material (Nasef, 2008):

1. Starting with a monomer containing ion exchange groups that can be copolymerized with non-functionalized monomer, to make ion exchange resins.
2. Starting with polymer pallet or powder, this can be modified by introducing of ionic characters directly or indirectly.

Among all preparation methods, radiochemical grafting (radiation-induced graft copolymerization) is a rather versatile method to produce tailor-made ion exchange resins. The attractiveness of this method arises from its ability to introduce desirable properties to pre-existing polymer host already having any physical shape without altering its bulk. Moreover, it offers the ability to closely control the graft copolymer compositions and properties by the selection of suitable grafting conditions.

Generally, radiation grafted ion exchange resins are mainly prepared by grafting of hydrophilic vinyl monomers onto hydrophobic polymer hosts. Irradiation of such grafting system causes a formation of free radicals on the polymer host, which can initiate copolymerization in the presence of monomer molecules. The polymer host could be a film, pallets or powder of either hydrocarbon or fluorocarbon polymer depending on the stability required for a certain application. The grafted monomers fall into two categories; reactive monomers such as acrylic acid and non-reactive monomers such as styrene. Grafting of acrylic acid directly confers a chemical functionality in a form of weakly acidic character ($-\text{COO}^-$) to the polymer backbone. Whereas, grafting of styrene leads to a formation of a chemically inactive graft copolymer, which has to be activated in a subsequent step to perform as a cation exchange resin (Nasef and Hegazy, 2004).

Sulfonation is the most common process to confer the graft copolymer a chemical functionality in the form of strongly acidic character (SO_3^-) in the resins. Sulfonation is commonly performed using strong sulfonating agent such as chlorosulfonic acid diluted with sulfonation resisting solvent (1,2-dicmethane,

1,1,2,2-tetrachloroethane or carbon tetrachloride) under controlled parameters (Nasef et al. 2003).

Numerous studies on preparation of cation exchange membrane by radiation-induced grafting have been reported, however, they concentrated on the introduction of weakly acidic ion exchange groups by grafting of acrylic acid onto a base film (Ishigaki et al., 1982; Hegazy et al., 1981, 1984; Gupta and Chapiro, 1989; Kostov, et al., 1992; Misra et al., 1995; Aouadj and Chapiro, 1996). However, radiation grafted resins containing strong acidic groups such as sulfonic acid groups have received less interest. This is most likely because monomers having sulfonic acid groups can not be directly grafted on hydrophobic polymer substrate as a result of the incompatibility between the highly ionized sulfonic acid groups with their hydration spheres and the polymer substrate. Therefore, a chemically inactive monomer such as styrene is commonly grafted onto the base films to produce graft copolymers having the capability to host sulfonic acid groups in a post-grafting reaction (Gupta et al. 1993).

The stability of radiation grafted resins relies strongly on the nature of starting polymer substrate. Among polymers, polyethylene (PE) films have been frequently used as a substrate for preparation of various ion exchange membranes. This is because of PE saturated structure, cheapness, resistance to solvents, high radiation resistance and excellent mechanical properties. A comprehensive review on the use of radiation induced grafting for preparation of cation exchange materials based on PE and other polymer films for various applications can be found in Nasef and Hegazy (Nasef and Hegazy, 2004).

1.2 Problem Statement

Environmental pollution by heavy metals from industrial streams is a serious problem that is receiving a lot of attention in many industrialized cities. The leakage of such metals to water has toxic effects on human and animal health and marine life. With the enactment of the "Clean Water Act" and its amendments, industry has been

required to meet even more stringent levels of water quality in their wastewater before discharge.

Current methods for industrial wastewater treatment include precipitation, coagulation/flotation, sedimentation, flotation, filtration, membrane process, electrochemical techniques, ion exchange, biological process, and chemical reaction. Each method has its merits and limitations in application. The ion exchange process with resins has been frequently used because of the effectiveness for the removal of heavy metal ions especially at trace quantities (Pohl, 2006). However, the operational cost of ion exchange process is high mainly due to the high cost of ion exchange resins which are controlled by few international manufacturers (Zagarondi, 2007). The search for an effective and economic method of removing toxic heavy metal ions requires the consideration of unconventional materials and processes. Preparing of these resins using simplified method starting from locally available polymer substrate would be very effective in reducing the cost such resins, improving the operational cost of waste water treatment in various industries and help in preserving the environment.

Radiation-induced graft copolymerization is a convenient method to convert polymer beads into ion exchange resins by direct introduction of chemical functional groups (Nasef and Hegazy 2004). This method has the merits of simplicity, controlled composition in graft copolymer, low cost and ability to start reaction with preformed polymers using various sources of radiations (electron beam, gamma rays irradiator and ion beam).

Petrochemical industry in Malaysia is rapidly expanding and producing a number of commodity plastics. Of them, polyethylene (PE) is produced massively and utilized in a wide number of industrial applications in the domestic market. Modifying these plastics by introducing ionic groups to become ion exchange resins is an interesting approach to add higher value to these plastics and diversify its applications.

1.3 Objectives of The project

1. To prepare strongly acidic cation exchange resins by radiation grafting method.
2. To optimize the reaction parameters by studying the effect of grafting conditions on the composition and the properties of the obtained resins.

1.4 Scope of the work

The scope of this work includes:

1. Grafting of styrene onto LDPE particles.
2. Studying the effect of grafting conditions on the degree of grafting.
3. Establishing the kinetics of the grafting reaction
4. Studying the effect of the variation of the degree of grafting on the properties of the obtained resins.

1.5 Report outline

This work probes the possibility of the development of strongly acidic cation exchange resins applicable for waste water treatment applications. In chapter I, an introduction to ion exchange resins including basic information about their types, methods of preparation and their applications are presented. A brief concept of concept of radiation induced grafting method is also highlighted. Moreover, the problem statement and the benefit of this work are also given. Chapter II reveals the basic fundamentals of radiation-induced graft copolymerisation processes and its application in the preparation of proton exchange resins together with a review of the previous studies on the preparation of radiation grafted cation resins for water separation and purification applications. The materials, equipments and methods used to prepare and characterise the proton exchange membranes produced in this study are described in Chapter III. The results concerning the effect of grafting conditions on the degree of grafting and the properties of the produced resins are presented and analysed in Chapter IV. Conclusions and recommendations for the future work are given in Chapter V.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The interest in water production has been dramatically increased in the recent years due to the shortage of water supplies in many areas and continuous diminishing of natural fresh surface water resources following the climate changes caused by the increase of green gas emission. Also, reliable production of high quality water for the process and power industries are one of basic requirements in modern industry, which have derived the progress in water purification technologies in many developing and industrialized countries.

The increase in using metals and chemicals in various process industries has resulted in generation of large quantities of effluents containing high level of toxic heavy metals and their presence poses environmental-disposal problems due to their non-degradable and persistence nature. Leaking of these heavy metals to the soil also poses a risk of contamination to groundwater and surface water. This could have adverse effects on human, animal and aquatic life. Environmental engineers and scientists are faced with the challenging task to develop appropriate low cost technologies for effluent treatment. Hence, the degree of sophistication of separation methods has increased tremendously.

Conventional methods for treatment of water and waste water including removal of metals from aqueous solutions involve various technologies such as chemical precipitation, chemical oxidation or reduction, ion exchange, filtration, electrochemical treatment, reverse osmosis, membrane technologies and evaporation

recovery (Dabrowski et al., 2004). Each method has its merits and limitations in application. Among all, ion exchange method and its associated electrochemical applications have been used successfully in many industries for more than fifty years for the removal of heavy metals from waste effluents of various characteristics (Nasef, 2008). This was prompted by the effectiveness of ion exchange processes for the removal of heavy metal ions and precious metals especially with large volumes containing trace quantities in addition to simplicity, elegance and range of variable reaction conditions (Pohl, 2006).

The advantages of ion exchange technology in water treatment processes can be summarized as follow: 1) capability of handling and separating components from dilute wastes, 2) possibility of concentrating pollutants, 3) capability of handling hazardous wastes, 4) possibility of recovery expensive materials from waste such precious metals, 5) possibility of regenerating ion exchanger and 6) possibility of recycling components present in the waste and/or regenerating chemicals (Wentz 1989). However, ion exchange processes have some limitations that include low concentration in the effluent to be treated, lack of selectivity against specific target ions, susceptibility to fouling by organic substances present in the wastewater and generation of waste as a result of ion exchanger regeneration and down time for regeneration upon using single column configuration (Metcalf and Eddy, 1991).

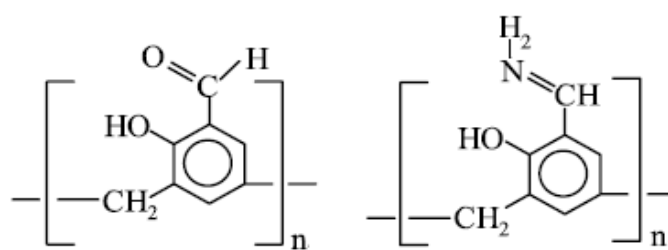


Figure 2.1: Phenol formaldehyde ion exchange resins.

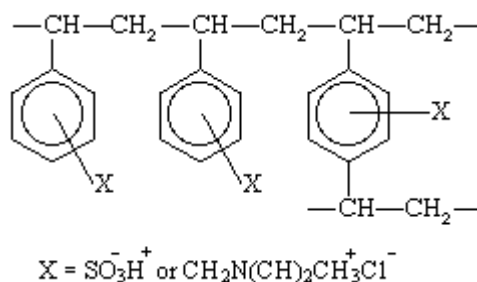


Figure 2.2: Strong cation and anion exchange resins based on polystyrene divinylbenzene copolymers.

2.2 Ion Exchange Materials

Commercial Ion exchange materials are available in different forms that vary in their classifications as shown in Figures 2.1 and 2.2. On the material origin basis, there is a wide variety of organic and inorganic ion exchange materials. Only cation exchange inorganic materials (for example zeolites and bentonites) are known. These materials compose of negatively charged porous structures with exchangeable cations located in internal voids. Unlikely, organic ion exchange materials can be both cation- and anion- exchangers and this classifies them based on the functional groups. Considering the separation function, ion exchangers can be classified into various categories including ion exchangers, chelating adsorbents, hydrogels, affinity polymers and polymer electrolytes.

On a material view point, organic (polymeric) ion exchange materials, which consist of functional groups bound to different polymeric frameworks available in various physical forms including hydrogels, resins, fibers, membranes and fabrics having widely differing chemical and physical properties. The majority of these forms have synthetic polymer structures i.e. such as polyethylene (PE), polystyrene (PS) and polyvinyl fluoride (PVF) while some of them are obtained from modified natural polymer sources including chitosan, starch, and cellulose. Various types of ion exchange membranes (schematized in Figure 2.3) are not only present in ion cation and anion exchange form but also in a bipolar or combined form containing

positively charge groups on one side and negatively charged groups on the other side forming a unique structure called amphoteric membranes. The separation behaviour of each type of these membranes is determined by the chemical nature of attached charged group. Unlike ion exchange membranes, resins follow the main two classes i.e. cation and anion exchange forms. A combination of cation and anion exchanges form can be used to obtain a combined bipolar form of the resins in a mixed bed column. More details on the various types of ion exchange materials can be found in the most regarded book on ion exchange materials was published by Helfferich (1962) and in the recent published book on the same subject by Zagorondi (2007).

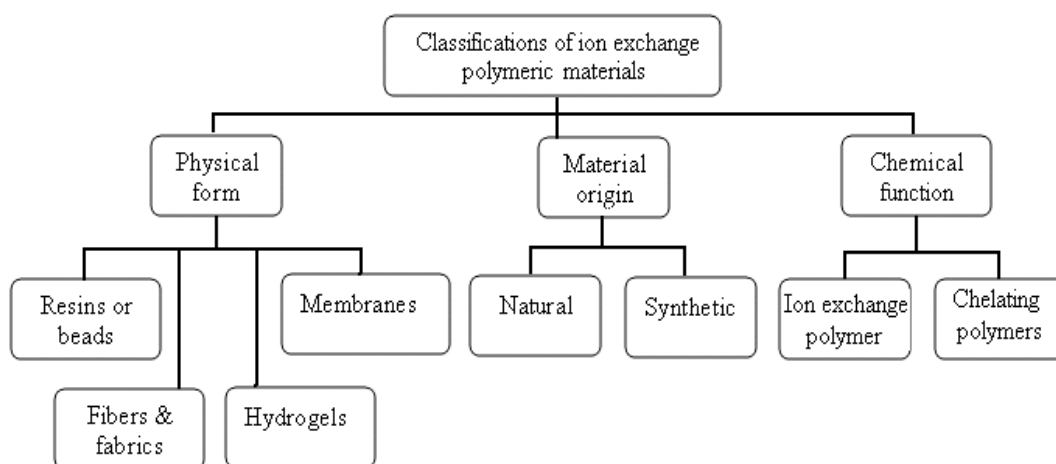


Figure 2.3: Schematic representation for various classifications of polymeric ion exchange materials.

Since ion exchangers act in a similar way to conventional acids and bases, the main classes of these materials i.e. cation- and anion exchangers can be further classified as follow: cation exchanges are divided into strong and weak cation exchangers depending on the type of functional groups attached to the polymer. Most typical strong acid exchangers contain sulfonic groups ($-\text{SO}_3^-$). Such materials are active over the entire pH range. Most weak acid exchangers have carboxylic groups ($-\text{COO}^-$). The weak acid exchangers are not active at pH values below 4-6 (this value significantly differs for various materials). However, they often have higher ion exchange capacities than the strong acid exchangers and have other specific advantages as well (Zagorodni, 2007).

The majority of strongly acid resins in use today have a styrene-divinylbenzene copolymer bead structure similar to that shown in Figure 2.2. This crosslinked structure gives the ion exchange resin beads certain physical properties including particle size and water swelling. Another important resin bead structure for water treatment resins is the acrylic resin structure. The operating properties for acrylic resins are different from those of an equivalent styrene divinylbenzene resin. One cannot say which resin structure is advantageous without knowing the site-specific operating conditions. The preferred resin is the one that has operating properties matching up best with the site's operating parameters, thus maximizing operating efficiency and cost effectiveness.

Strongly acid resins are commonly used in water softening and demineralization applications. In softening applications, the resin is used in the sodium form (regenerated with salt) and in demineralization applications the resin is used in the hydrogen form (regenerated with acid). These resins also can be used in a split-stream dealkalization process. These resins can be purchased with different percentages of crosslinking. The common crosslinking level in these resins is 8 percent crosslinked. However, higher and lower crosslinked resins are also available with less or more water content. On the other hand, weak acid cation resins can be used in demineralization and dealkalization systems. They are very efficient when matched up with the proper influent water chemistry.

Anion exchangers are classified in a similar way into strong base anion exchangers and weak base anion exchangers. Strong base exchangers have quaternary ammonium groups ($-\text{NR}_3^+$). They are active over the entire pH range. Weak base exchangers have primary ($-\text{NH}_2$), secondary ($-\text{NRH}$), and/or tertiary ($-\text{NR}_2$) amine groups. The weak base exchangers are not active at alkaline pH. However, they are advantageous in many practical cases. Strong base anion resins are used in ion exchange demineralization, dealkalization, desilicization processes and also in organic trap applications.

Unlikely, weak base anion exchange resins can not be used for demineralization as they allow the carbonate/bicarbonate and silica ions to pass through. Therefore, they have to be used with strong base resin to consider such

application. However, weak base resins can remove the anions of the strong mineral acids (sulfate, chloride and nitrate). A summary of the common functional groups and their negative logarithm of the dissociation constant (pK) is presented in Table 2.1. It can be clearly seen that each of these major resin classes has several physical or chemical variations within the class. The variations impart different operating properties to the resin.

With the wide number of resin types available in the marketplace, it is highly possible that there is more than one technically effective solution that meets all the system's design specifications. To have a robust ion exchange system design a thorough knowledge of all available resin types along with their various advantages and disadvantages to ensure the efficiency and cost effectiveness of the ion exchange system.

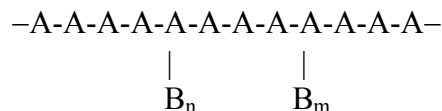
Table 2.1: Common functional groups of polymeric ion exchange materials and their respective pK values.

Cation exchange materials		Anion exchange materials	
Functional groups	pK	Functional groups	pK
$-\text{SO}_3\text{H}$ (strong acidic)	1–2	$\equiv\text{N}^+$ (strong basic)	1–2
$-\text{PO}_3\text{H}_2$	2–5	$=\text{N}$	4–6
$-\text{COOH}$	4–6	$=\text{NH}$	6–8
$-\text{OH}$ (weak acidic)	9–10	$-\text{NH}_2$ (weak basic)	8–10

2.3 Graft Copolymerisation

Graft copolymerisation is a well-known method for modification of chemical and physical properties of polymeric materials such as films and fibers. This method is of particular interest for achieving desired membrane properties since various commercial base polymers can be used as grafting substrates (Hegazy et al., 1986 a).

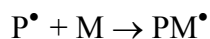
In principle graft copolymerisation is the process in which side chain grafts are covalently attached to the main chain of a polymer matrix to form branched copolymer (Billmeyer, 1984). A graft copolymer can be represented as follows:



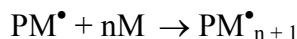
where, A is the main chain, B_n and B_m are the side chain grafts. Both the backbone and side chain grafts can be homopolymers or copolymers (Stannett, 1981). This process takes place as a result of formation of active sites on the polymer backbone. The active sites may be free radicals or ionic chemical groups, which initiate the polymerisation reaction. The formation of active sites on the polymer backbone can be carried out by several methods such as mechanical, chemical, photochemical and radiochemical methods (Battared and Tregear, 1976; Chapiro et al., 1976). Of these methods, radiochemical is very suitable, specially, when starting polymers are not reactive towards most chemical agents (Elmidaoui, 1992). In this method active sites are formed on the polymer backbone by irradiation and are allowed to react with a monomer, which can then propagate to form side chain grafts. The overall graft copolymerisation process involves three main steps and may be represented as follows:

Initiation:

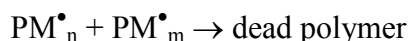
γ -ray



Propagation:



Termination:



where, P^\bullet is the primary radical site, PM^\bullet is the initiated chain, M is the monomer unit and PM_n^\bullet as well as PM_m^\bullet are the graft growing chains. Any parameter that affects one or more of these steps results in a variation in the degree of grafting.

However, attention is essentially confined to the first step where radiation can be often considered as an alternative to chemical initiation by activated catalyst (Charlesby, 1991).

2.4 Radiation-induced Grafting

Radiation-induced grafting using high-energy radiation offers an attractive and practical technique for preparation of permselective membranes for various applications (Chapiro, 1983). The use of such polymerization technique was started in 1950s and has been continued extensively until now. Cobalt-60 and electron beam generators are the main sources of high-energy radiation for such technique (O'Donnell, 1989; Reichmanis et al., 1993). This technique has the potential to simplify the whole treatment process, leaves no detrimental residue and reduces the cost of production (Dessouki et al., 1990). It also has the ability to initiate polymerisation in a wide range of temperatures including low region in various states of monomers such as in bulk, solution, emulsion and even at solid state (Tabata, 1991). Moreover, it offers a unique way to combine two highly incompatible polymers and imparts new properties to the resulting graft copolymers (Okamoto, 1987). The versatile nature of this technique is attributed to the ability to control the degree of grafting by the proper selection of the irradiation conditions (Chapiro, 1962). Therefore, this process could be used for a wide range of polymer-monomer combinations and offers tailor-made polymers for specific applications. For applications which require thin membranes, this technique shows a superior advantage where the difficulty of shaping the graft copolymer into a thin membrane of an uniform thickness could be circumvented by the possibility of starting the process with a thin film already having the physical shape of a membrane (Gupta et al. 1993; Xu et al., 1983).

2.5 Types of Radiations

Different types of high-energy radiation are available for graft copolymerisation processes (Ivanov, 1992). They can be classified into electromagnetic radiation (photons) such as γ -rays and x-ray, and particulate radiation (charged particles) such as electrons and β -particles. The radioactive isotopes such as Cobalt-60 and Cesium-137, which are fission products of nuclear plants, are the main sources of γ -radiation. However, Cobalt-60 is more advantageous and has been widely used due to higher energy emission (1.25 MeV compared to 0.66 MeV for Cs-137), ease of preparation and low cost (Mehnert et al., 1993).

Two different types of γ -radiation sources are commercially available; a laboratory scale known as 'Cavity-type' and industrial one known as 'Cave-type'. In the first type, the Cobalt-60 unit forms a hollow fixed cylinder in which samples can be introduced to radiation from the source by means of a mobile drawer. This unit is provided with lead shielding to prevent the escape of radiation. Whereas, in the second type, Cobalt-60 unit is mobile and normally kept in a shielded container of concrete and the whole system is preserved underground or under water. Fixed samples can be irradiated through the movement of the Cobalt-60 unit with the help of a belt.

Particulate radiations such as electrons are normally obtained from accelerators, which give electron beams with energy in MeV range. A large number of linear accelerator are commercially available and can produce electrons having energies in the range of 1-6 MeV. More specific information about various types and sources of radiation can be found elsewhere (Chapiro, 1962; Ivanov, 1992; Mehnert et al., 1993).

From the grafting point of view, electromagnetic radiation is more advantageous in terms of high penetration power compared to particulate radiation (Luig et al, 1993). Upon crossing the matter, the charged particles lose energy continuously through a large number of small energy transfers. Whereas,

electromagnetic radiation tend to lose a relatively large amount of their intensity by interaction with the matter. The fractions of photons that do not interact with the finite thickness of the matter are transmitted with their original energy and directions. Therefore, the dose rate can be easily controlled by the use of suitable attenuator without influencing the photon energy, which is very important aspect in radiation-induced grafting (Gupta and Scherer, 1994). The most widely used attenuator for γ -radiation is lead, which exhibit lower thickness as compared to other attenuators. Finally, γ -radiation is normally utilized for fundamental studies and for processes, which include low-dose rate of irradiation with deep penetration.

The energy absorption has been traditionally expressed as dose in 'rad', which is the measure of energy deposition in one gram of the matter and equals to 10^2 erg/g or 10^{-2} J/kg. The most recent unit (SI system) is the Gray (Gy), which is equal to 10^4 erg/g or 1 J/kg. So, the dose rate, which is the absorbed dose per unit time, can be expressed as Gy/s and kilo-gray (kGy) is used to express the large amount of radiation doses. However, some sources still continue to use the old unit Megarad (Mrad), which is equal to 10 kGy, as a dose expression (Lyons, 1997). Radiation yields are traditionally expressed as G-value for numbers of molecules changed per unit energy absorbed (100eV) (O'Donnell 1989). The new energy unit for G-value is expressed in micro-moles per joule (μ mol/J).

The molecular changes in polymers resulting from radiation-induced chemical reactions may be classified as: i) Chain cross-linking, causing increase in molecular weight and the formation of microscopic network. ii) Chain scission, causing decrease in molecular weight and thus substantially changes the polymer material properties. iii) Small molecule products, resulting from bond scission followed by abstraction or combination reactions. iv) Structural changes in the polymers, which accompany the formation of small molecule products from the polymer (Reichmanis et al., 1993).

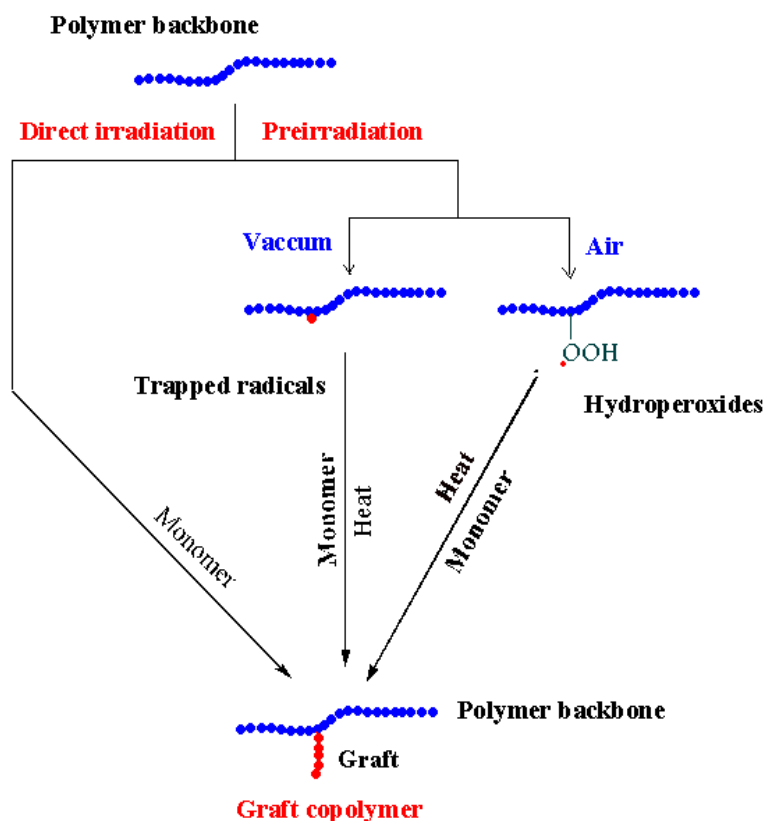


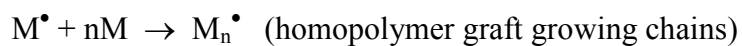
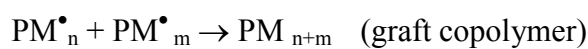
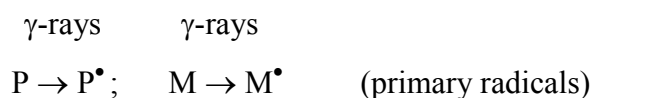
Figure 2.4: A schematic representation of various method or radiation induced grafting.

2.6 Different Methods of Radiation-induced Grafting

The first methods for radiation-induced graft copolymerisation were reported 40 years ago. Since that time, various techniques have been developed for grafting of a wide variety of monomers onto a number of polymer backbones (Charlesby, 1960; Stannett, 1981,1990). The most recent research in radiation-induced graft copolymerisation involved two main methods. They are simultaneous (direct) irradiation and preirradiation (post-irradiation) methods, which can be performed either in presence of air or under vacuum (Chapiro, 1962; Tabata, 1991). A general schematic representation of the radiation-induced grafting methods is shown in Figure 2.4.

2.6.1 Simultaneous Irradiation Method

This is the simplest irradiation technique for the preparation of graft copolymers. In this method, a polymer backbone is irradiated in the presence of a monomer which can be used in a vapour, liquid or solid form. Irradiation may take place in air, inert atmosphere or preferably under vacuum leading to the formation of active free radicals on both the polymer backbone and the monomer units. The reaction between the monomer unit and the polymer backbone to form graft copolymer can be represented as follows:

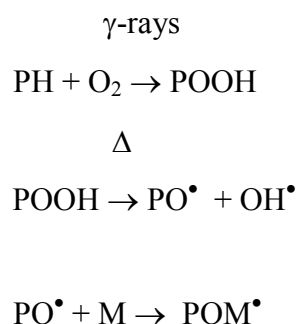


where, P is the polymer backbone and M is the monomer unit while P^\bullet and M^\bullet are the primary radical sites of the polymer and the monomer unit, respectively. PM_n^\bullet and PM_m^\bullet are the growing chains of the copolymer. M_n^\bullet and M_m^\bullet are the growing chains of the homopolymer. The graft growing chains of homopolymer terminate either by combination or disproportionation (Chapiro, 1977). Although, the simultaneous irradiation method is the most efficient in principle, it has some limitations such as the formation of homopolymer. However, a number of suitable conditions can be applied to reduce the effect of homopolymer formation and consequently improve the grafting efficiency. These conditions include the addition of polymerisation inhibitors such as Fe^{++} and Cu^{++} salts, the use of good swelling agents, selection of low dose rate to avoid the rapid termination of grafting chains

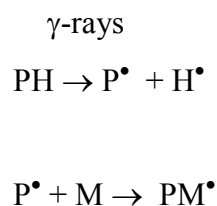
and the addition of the monomer either in vapour or liquid form to the polymer while it is in a solid form (Stannett, 1981, 1990). The reason behind applying such conditions is to keep the formation of radicals in polymer backbone higher than that in monomer units and thereafter more monomer units contribute to the graft copolymerisation than homopolymerisation (Ellinghorst et al., 1983; Stannett, 1990).

2.6.2 Preirradiation Method

Preirradiation method involves a combination of two steps; 1) irradiation of the polymer backbone to form active free radicals and 2) contact of the irradiated polymer backbone with monomer units. If irradiation step is carried out in air, the generated radicals react with oxygen to form peroxides and hydroperoxides. Upon contacting with monomer units, graft copolymerisation is initiated by thermal decomposition of hydroperoxides. The overall reaction is suggested as follows (Chapiro, 1977, Bozzi and Chapiro, 1987):



On the other hand, if irradiation is carried out under vacuum or in an inert atmosphere, the generated radicals on the polymer backbone remain trapped and initiate grafting in the presence of monomer units according to the following reactions:



The stability of P^\bullet and PM^\bullet mainly depends upon the crystallinity of the polymer backbone, temperature, and storage period of the irradiated films. Thus far, it is not directly known which one of the two irradiation methods is superior (Tabata, 1991). In practice, the preirradiation method has been given much attention because the homopolymer formation is little and the grafting can be carried out at any time, away from radiation sources (Dworjanyn and Garnett, 1992).

2.7 Radiation-induced Grafting for Preparation of Ion Exchange Resins

Synthetic polymeric resins play a very important role for practical applications in various separation and purification processes. In spite of their good separation properties, these research have short comings as far as their selectivity, chemical and thermal stability are concerned. Considerable efforts have therefore been spent in the recent years to develop new resins with better separation characteristics and tailor-made properties for specific applications. The use of radiation-induced grafting has been found to be a convenient mean for the preparation of tailored permselective membranes. By grafting of different monomer/polymer combinations, various types of membranes suitable for various fields of applications can be produced.

In this respect, graft copolymerisation of hydrophilic (vinyl) monomers onto hydrophobic base polymers has been used to prepare cation exchange membranes. The grafting monomers fall into two categories; 1) functionalised monomers such as acrylic acid and 2) non-functionalised monomers such as styrene and its derivatives. Graft copolymerisation of acrylic acid directly confers weakly acidic character to the polymer backbone (Ishigaki et al., 1977; Hegazy et al., 1981 a, b; Gupta and Chapiro, 1989 a; b). Whereas, graft copolymerisation of styrene leads to the formation of chemically inactive (neutral) graft copolymers, which have to be chemically activated by introducing of chemical groups in a subsequent step to make them perform as cation exchange membrane. Sulfonation is the most common process to confer the graft copolymers strongly acidic characters (Tsuneda et

al.1995). The basic fundamentals for the preparation of radiation grafted acrylic as well as sulfonic acid cation exchange membranes and their latest application can be found in the comprehensive review revealed by Gupta and Scherer (1994).

The first radiation grafted cation exchange membrane was prepared by radiation graft copolymerisation of styrene onto polyethylene film (PE) followed by sulfonation reaction (Chen, et al.,1957). Later, various membranes have been prepared by extending the same idea to various polymer/monomer combinations using both simultaneous and preirradiation techniques (Munari, 1967; Momose et al., 1989 a, b; Xu et al., 1993; Büchi et al., 1992; Röully et al.,1993; Gupta et al., 1993; Gupta et al., 1994 e; 1996 b; Holmberg et al. 1996, 1998; Flint and Slade, 1997, Brack et al. 1998; Holmberg et al. 1998).

2.8 Factors Affecting the Degree of Grafting

There are many factors that strongly affect radiation-induced graft copolymerisation process and subsequently the grafting yield (degree of grafting). Variation of such factors causes considerable changes in the degree of grafting of the graft copolymer. Consequently, a real possibility to closely control the compositions of membrane as well as its properties is obtained (Chapiro, 1962). These factors include the irradiation dose and dose rate, nature of the monomer, nature of the base polymer, monomer concentration, type and concentrations of additives such as diluent, crosslinking agent and inhibitor, grafting temperature and irradiation atmosphere.

2.8.1 Irradiation Dose and Dose Rate

Both irradiation dose and dose rate have considerable effect on the degree of grafting. The former influences the amount of generated radicals in the grafting system while the latter influences the survival of such radicals as well as graft

growing chains (Chapiro, 1969; 1962). Generally, higher irradiation doses lead to higher degrees of grafting. This is due to the enhancement of free radical formation in the grafting system. In contrast, higher dose rates result in lower degrees of grafting. This is attributed to enhancement of radicals' recombination and fast termination of graft growing chains (El-Assy, 1991). It is important to mention here that the irradiation dose is a function of grafting time in simultaneous irradiation, whereas in preirradiation, irradiation dose and grafting time are two independent parameters.

2.8.2 Nature of the Monomer

The nature of the monomer to be grafted onto a base polymer has an important effect on the efficiency and uniformity of the degree of grafting (Dole, 1973). Based on the reactivity and the sensitivity to radiation, monomers can be classified into two classes; reactive and non-reactive (inert) monomers. Reactive (radiation-sensitive) monomers such as acrylic acid shows a high tendency to form homopolymers while that for non-reactive monomer such as styrene is lower. Therefore, an inhibitor has to be added to the reactive monomers to reduce the homopolymerisation effect. Furthermore, monomers to be grafted should have low viscosity and small dipole strength (Dole, 1983). The former enhances the amount and the rate of monomer diffusion into the base polymer while the later reduces the tendency of the monomer to form free radicals. Since simultaneous radiation-induced grafting includes radical formation onto both monomer and base polymer, the highest degree of grafting is obtained when the number of free radicals formed on the base polymer is much greater than on the monomer (Abdel-Bary and El-Nesr, 1997).

2.8.3 Nature of the Base Polymer

The nature of the base polymer to be used in radiation graft copolymerisation is very critical in the determination of the conditions of the radiation-induced grafting process (Stannet, 1981). Particularly, the sensitivity of these polymers towards radiolytic degradation has to be considered before the selection the irradiation dose and dose rate (Gupta et al., 1994 d). Such polymers have to meet certain requirements in order to produce efficient graft copolymers with desirable and practical properties. They have to bear the ability to easily generate stable free radicals upon exposure to high-energy radiation and high resistance towards radiolytic degradation (Chapiro, 1962). Preferably, base polymers also have to be hydrophobic materials of high thermal, chemical and mechanical stability (Gen, 1987). In this respect, fluorine containing polymers have shown outstanding thermal, chemical and mechanical stability (Lyons, 1995). Besides, they also have shown the ability to produce highly stable radicals compared to conventional hydrocarbon polymers such as polyethylene and polypropylene upon exposure to high-energy radiation (Gupta et al., 1996 a). Such advantages have given them extensive uses in a wide range of different applications (El-Assy and Dessouki, 1987; Hegazi et al., 1989 a; 1990; Abdel-Gaffar et al., 1990 ; Kostov et al., 1992).

2.8.4 Monomer Concentration

The concentration of monomer has a significant effect on the degree of grafting in radiation-induced graft copolymerisation process. In general, an increase in the monomer concentration at given grafting time causes an increase in the rate and the degree of grafting. However, the final degree of grafting as well as the rate of grafting normally tends to level off and approach saturation with longer irradiation time at certain monomer concentration. Beyond this concentration, further increase in the monomer concentration causes sharp fall in the degree of grafting (Hegazy et al., 1986 b; Ishigaki et al., 1982). Such sharp fall mostly takes place in both the rate of grafting and the final degree of grafting and can be attributed to the decrease in the monomer concentration and its diffusion in the grafting layers which reaches maximum swelling. In some grafting systems where the polymer substrate scarcely

swells in the grafting mixture, such effect is attributed to the suppression of the monomer diffusion by the increase in the viscosity of the grafting mixture under the effect of homopolymerisation. Therefore, graft copolymerisation largely depends on the availability of the monomer in the grafting sites and simply it is a diffusion-controlled process.

2.8.5 Type of Diluent

Diluents are basically used in radiation-induced graft copolymerisation processes to bring about swelling of the base polymer and hence enhance the monomer accessibility to the grafting sites (Garnett and Martin 1976). Therefore, the correct choice of diluent is one of the essential elements towards the success of radiation-induced grafting process (Kabanov et al., 1980). The influence of the diluents on the radiation graft copolymerisation has been subjected to many studies (Omichi and Okamoto, 1982; Omichi and Stannett, 1985). It has been established that nature of the diluent not only determine the degree of grafting but also the location of grafting (Stannet, 1981). If poor-swelling diluent is used surface grafting is most likely to take place due to the slow down in monomer diffusivity and eventually, low degrees of grafting are obtained. However, if good-swelling diluent is used bulk grafting is highly favoured and homogeneous grafting is obtained. The increase in the swelling enhances the diffusion of monomer to the internal layers of the polymer substrate and hence increases the interactions between internal active sites and the monomer molecules leading to a homogeneous grafting as well as higher degrees of grafting (Dessouki, 1987; Hegazy et al., 1986 a).

2.8.6 Addition of Crosslinking Agent

Crosslinking agents or crosslinkers are polyfunctional monomers having at least two double bonds in their chemical structure such as divinylbenzene and triallylcyanorate. Crosslinking agents are normally added to the grafting medium to

maintain certain desirable properties in the grafted film such as mechanical properties (Zundel, 1969; Dardel and Arden, 1993). However, the addition of crosslinking agents leads to a decrease in the degree of grafting and an enhancement in homopolymerisation (Gupta et al., 1994 e; Büchi, et al., 1995 a). This can be attributed to the reduction of the polymer chain mobility and its swelling as well as the monomer diffusibility. To overcome such a problem, the grafting process has to be carried out for a longer time and the amount of the cross-linking agent has to be optimised to get comparable degree of grafting (Gupta et al., 1994 e). Comprehensive reviews of radiation crosslinking of polymers and fluoropolymers in particular can be found in Lyons (1984; 1995; 1997).

2.8.7 Grafting Temperature

The temperature of the grafting reaction has shown to have a significant effect on the grafting process (Ishigaki et al., 1982; Momose et al., 1989 a, Ivanov, 1992). At high temperature the initial rate of grafting increases, however the final degree of grafting decreases (Hegazy et al., 1981a; Gupta and Chapiro, 1989 a, b ; Gupta et al., 1994 e). Such behaviour was found to be similar to grafting of styrene as well as acrylic acid onto fluorinated films using preirradiation technique (Gupta and Scherer, 1994). This is most likely attributed to the enhancement of the monomer diffusibility into the polymer matrix as well as the reactivity of trapped radicals causing an increase in the initial rate of grafting (Hegazy et al., 1981 a, b; Gupta and Chapiro, 1989 a,b ; Gupta et al., 1994 e). After certain time of grafting, the accumulation of the grafted monomer on the surface layers of the polymer backbone hinders the monomer diffusivity resulting in an insufficient monomer concentration to react with the active radicals. Thereby, fast termination of the growing chains takes place and the final degree of grafting decreases. In contrast, at low temperature, the trapped radicals have longer lifetime and lower reactivity. This causes a slow down in the growing chain termination and subsequently higher grafting yield is obtained.

2.8.8 Addition of Acids

Acids are usually added to grafting mixtures to enhance the degree of grafting and consequently improve the economy of the grafting process. The addition of mineral acids to increase the grafting yield was found to affect a variety of base polymers and therefore, the use of acid to enhance radiation-induced graft copolymerization became applicable to wide range of grafting systems (Garnett et al. 1985; Gupta and Chapiro, 1989 a; Al-Assy 1991). In particular, this concept is valuable when low dose is required to achieve certain degree of grafting in the membranes. The effect of acid addition was found to be pronounced at the Trommsdorff peak while it remains low at concentration of monomer above and below this point (Dargaville et al. 2003).

The use of acid as an additive when grafting to polyolefins polymers has received much attention in literature (Dworjanyn and Garnette, 1992). For example, the addition of little amount of sulfuric acid is found to accelerate grafting of acrylic acid (Gupta and Chapiro, 1989) and acrylonitrile (Choi and Nho 2000) onto PE films. The addition of little amount of organic acids (acetic, oxalic, formic) was also found to enhance the degree of grafting of styrene in benzene, toluene and methylene chloride onto PE films using simultaneous irradiation technique (Al-Assy, 1991).

The enhancement of grafting yield in systems containing polyolefins by acid addition was initially explained on the basis of the assumption that the presence of acid facilitates the hydrogen abstraction from the adjacent polymer molecule by monomer-solvent radicals during the grafting reaction (Chapiro 1959). Subsequently, considerable research work by Garnett and coworkers showed that the acid enhancement of grafting was attributed to partitioning effect. The acid was found to modify the partition coefficient of the styrene between the polymer film and the external liquid phase leading to an increase in the local styrene concentration around the graft growing chains i.e. the concentration of the absorbed styrene becomes higher than its corresponding one in the bulk solution (Garnett et al. 1975; 1985).

The acid enhancement is most effective when non-polar are grafted onto non-polar substrates with methanol as a solvent (Garnett et al. 1990). The greater polarity of methanol containing dissolved acid favors the partitioning of the non-polar styrene into the substrate. Conversely a polar monomer would not be salted-out and the increase in diffusion of the monomer to the grafting sites would not happen (Dargaville et al. 2003).

The addition of acids to fluorocarbon polymers was subjected to little investigations (Nasef 2001). Unlike grafting onto polyolefins, the addition of a series of mineral and organic acids was found to have no effect on the grafting of styrene in various solvents (methanol, benzene and methylene chloride) onto PTFE, FEP and PFA films (Nasef, 2001). On contrast, the addition of unspecified acid during grafting of styrene/2-hydroxyethyl methacrylate mixture in methanol to PTFE using simultaneous irradiation method was found to bring slight but definite increase to the grafting yield (Dworjanyn et al. 1993).

CHAPTER 3

METHODOLOGY

3.1 Materials

LDPE resins were obtained from Petronas Inc. Malaysia. Styrene of purity more than 99 % was purchased from Fluka (Switzerland) and used without any further purification. Chlorosulfonic acid of analytical grade (Fluka) was used. Solvents: Toluene (J.T. Baker) 1,2-dichloromethane (J.T. Baker) and 1,1,2,2-tetrachloroethane (Fluka) were reagent grades and used as received.

3.2 Preparation of Cation Exchange Resins

The resins were prepared following the two-step procedure involves: 1) grafting of styrene onto LDPE resins under controlled conditions followed by 2) sulfonation reaction to confer the grafted resins their cation exchange characteristics.

3.3 Grafting of Styrene

LDPE resins of known weight were placed in a glass ampoule containing styrene monomer of desired concentration diluted in with a solvent. Additives such as acids were added upon desire. The air was removed from the grafting mixture by

flushing the ampoule with purified N₂ for 10 minutes. The ampoule was then sealed and irradiated using γ -rays from a ⁶⁰Co source of dose rate of 1.32 kGy/h to prescribed time. After completion of the grafting, the grafted resins denoted as LDPE-g-PS were extracted, washed with toluene and soaked therein overnight to remove the excess monomer and homopolymer from the film surfaces. The effects of various grafting parameters namely, monomer concentration, irradiation dose, dilution solvent and addition of acid for grafting of styrene onto LPPE on the degree of grafting and the properties of the obtained graft copolymer films were investigated. The degree of grafting was determined as the weight gain according to the following equation:

$$\text{Degree of grafting(\%)} = \frac{W_g - W_0}{W_0} \times 100 \quad (4.1)$$

where, W_g and W₀ are the weights of pre-grafted and grafted PE films, respectively.

3.4 Sulfonation

Clean and dried LDPE-g-PS resins were placed in a glass reactor filled with the sulfonation mixture composing of 30 parts chlorosulfonic acid in 70 parts of 1,1,2,2-tetrachloroethane (v/v). The reaction was allowed to continue for 2 hours at room temperature with occasional stirring under nitrogen atmosphere. The sulfonated resins were removed from the reactor, washed several times with 1,1,2,2-tetrachloroethane and dichloromethane to remove the excess of sulfonic acid. The membranes were then hydrolyzed with 0.5 M KOH solution overnight and regenerated into acid form by boiling with 1M HCl for 2 hours. The samples were then washed free of excess HCl with deionized water 4 times.

3.5 FTIR Spectral Analysis

FTIR analysis was conducted using Perkin Elmer spectrometer (Spectrum 2000 Explorer) spectrophotometer at ambient conditions in transmittance mode. The spectra were detected by ATR accessory equipped with Zn Sn lens at fixed angle of 45° . The original, grafted, sulfonated LDPE resins were hot pressed at 110°C into films prior running FTIR spectral analysis.

3.6 Determination of Ion Exchange Capacity

Ion exchange capacity (IEC) of the resins was determined by back titration. Membrane samples in acid form were immersed into 0.5 M KCl solution overnight at room temperature. The protons (H^+) released in the solution were titrated against standardized 0.05 M KOH solution by an automatic titrator (Metrohm, Switzerland) until pH 7 was reached. IEC per unit mass of the dry membrane (mmol/g) was calculated from the volume KOH solution consumed in titration after taking the weight of the dry membrane into account. The theoretical ion exchange capacity was calculated based on the assumption that the ratio of sulfonic acid groups to aromatic rings equal to unity.

3.7 Evaluation of Swelling Behavior

The swelling of the resins was determined by calculating the water uptake and the number of water molecules per sulfonic acid group ($\text{nH}_2\text{O}/\text{SO}_3^-$). Dry membrane samples in the acid form were immersed in boiling deionized water until swelling equilibrium was achieved. The membrane samples were removed, the excess of water adhering to the surface was quickly blotted by absorbent papers and

then the samples were weighed. The membrane water uptake was calculated using equation 2:

$$W (\%) = [(W_w - W_d)/W_d] \times 100 \quad (4.2)$$

where, W_w and W_d are the weights of wet and dried membranes, respectively.

3.8 X-Ray Diffraction (XRD)

XRD measurements were performed using Philips, PW 1830, x-ray diffractometer. The diffractograms were measured at ambient temperature and 2θ in the range of $5-50^\circ$ by means Cu-K α radiation ($\lambda=1.54$) monochromated by means of Nickel filter.

3.9 Differential Scanning Calorimetry (DSC)

Perkin Elmer, Pyris-1 DSC was used to obtain the thermograms of the membranes. The membrane samples were initially dried at 60°C in a vacuum oven (10^{-4} torr) for 24 h and stored under desiccator over fresh silica gel prior to DSC runs. The samples were analyzed over a temperature range of $50-180^\circ\text{C}$ at a constant programmed heating rate of $20^\circ\text{C min}^{-1}$ and under nitrogen atmosphere.

3.10 Calculations of the Degree of Crystallinity

The degree of crystallinity of the original PE (as received) resin was calculated using equation 2.

$$\text{Degree of crystallinity (\%)} = (\Delta H_m / \Delta H_{m100}) \times 100 \quad (4.3)$$

where, ΔH_m is the heat of melting of PE resin and ΔH_{m100} is the heat of melting of 100 % crystalline PE polymer which equals 290 J/g (23).

Since the incorporated polystyrene has an amorphous nature, the crystallinity in the grafted PE films (PE-g-PS) and in the final sulfonated resins (PE-g-PSSA) is always referred to the fraction of PE matrix.

The crystallinity of PE-g-PS films is calculated using equation 2 after correcting the recorded ΔH_m by dividing over the weight fraction of PE in the grafted film [$W_{PE(PE-g-PS)}$] obtained from equation 3:

$$W_{PE(PE-g-PS)} = m_{PE} / (m_{PE} + m_{PS}) \quad (4.4)$$

where, m_{PE} and m_{PS} are the weight fractions of PE and grafted polystyrene, respectively.

Similarly, the degree of crystallinity of PE-g-PSSA resins is calculated using equation 2 after taking into the account the weight fraction of PE in the resins [$W_{PE(PE-g-PSSA)}$] calculated using equation 4.5:

$$W_{PE(PE-g-PSSA)} = m_{PE} / (m_{PE} + m_{PSSA}) \quad (4.5)$$

where, m_{PSSA} is weight of sulfonated polystyrene grafts, which equals $m_{PS} + m_{SO_3^-} + m_{H_2O}$.

3.11 Thermal Gravimetric Analysis

Thermal stability of the resin was tested by thermal gravimetric analysis (TGA), which was performed using Perkin-Elmer TGA-7. Thermograms were obtained for samples of vacuum dried membrane, original and grafted FEP films having typical weight of 10-20 mg in a temperature range of 50-600 °C. All TGA runs were made at a constant heating rate of 20°C/m in nitrogen atmosphere.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effect of Grafting Conditions

Preparation of sulfonic acid cation exchange resins was carried out in two-steps procedure where styrene was first grafted onto LDPE granular particles under controlled conditions followed sulfonation with chlorosulfonic acid. The grafting of styrene was carried out onto LDPE resins under various reaction conditions in order to determine the optimum conditions that can be used to obtain desired degree of grafting. The investigated grafting conditions include irradiation time, monomer concentration, addition of inhibitor, type of solvent, addition of acid, irradiation dose, dose rate. Details of the effect of every investigated parameter are discussed in next sections.

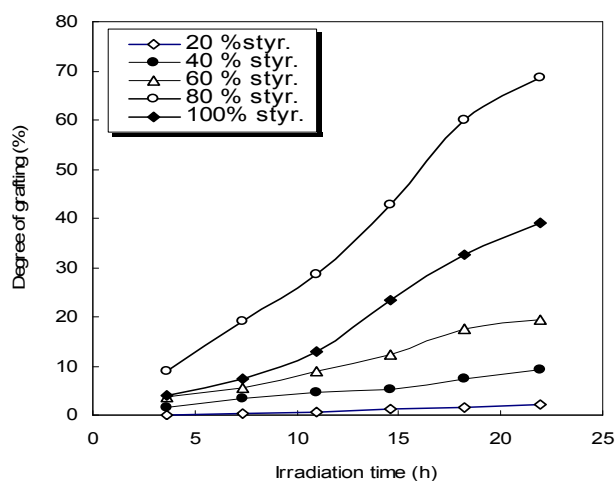


Figure 4.1: The degree of grafting vs. irradiation time at various styrene concentrations.

4.2 Effect of Irradiation Time

Figure 4.1 shows the relationship between the degree of grafting and irradiation time at various styrene concentrations (20-100 vol %) in dichloromethane. It can be seen that the degree of grafting increases with the irradiation time for all styrene concentrations and tends to level off at longer irradiation time. Moreover, the degree of grafting increases as styrene concentration increases and reaches its maximum value at 80 vol%. However, further increase in styrene concentration causes a sharp fall in the degree of grafting. This phenomenon is most likely attributed to the increase in the viscosity of the grafting mixture due to homopolymerization effect, which reduces the diffusibility of the monomer and its concentration in the grafting layers. These results are in a good agreement with those reported by Hegazy et al. (1986) and Dessouki (1987) upon grafting of 4-vinylpyridene and vinyl acetate onto PE films, respectively.

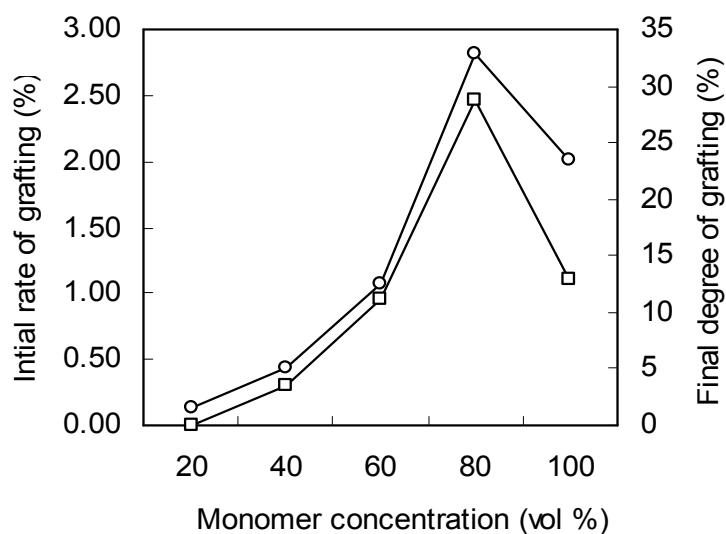


Figure 4.2: The initial rate of grafting as well as the final degree of grafting vs. the styrene concentration.

4.3 Effect of Monomer Concentration

Figure 4.2 shows the relationship between the initial rate of grafting as well as the final degree of grafting and the styrene concentration. As can be seen, both the initial rate of grafting and the final degree of grafting increase with styrene concentration up to 80 % beyond which it drops sharply. These results suggest that, the degree of grafting of styrene onto LDPE is not only depending upon the amount of trapped radicals but also upon the diffusibility of styrene through the polymer matrix and the styrene concentration in the grafting layers as well. These results also suggest that, the grafting starts at the surface of particles and proceeds internally by successive diffusion of the styrene until equilibrium swelling is reached at 80 % monomer concentration. A similar trend was reported by Ishigaki et al. (1982) in the radiation grafting of acrylic acid onto PE films but these authors found a maximum in the rate of grafting was achieved at a monomer concentration of 60 %.

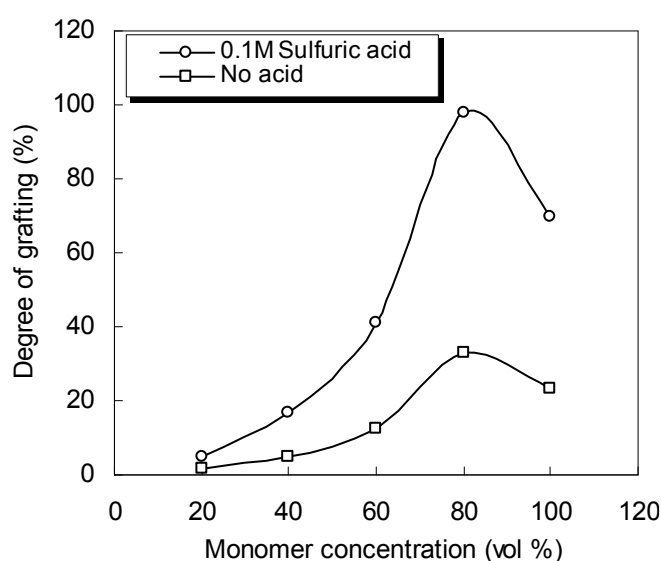


Figure 4.3: The degree of grafting vs. the styrene concentration with and without sulfuric acid addition.

4.4 Effect of Acid Addition

Figure 4.3 shows the degree of grafting versus the styrene concentration with and without sulfuric acid addition. It can be clearly observed that the sulfuric acid

addition remarkably enhances the degree of grafting of styrene onto LDPE and the degree of grafting increases with the increase in the styrene concentration. Garnett et al. (1974) early explained this behaviour on the basis of the assumption that the presence of acid facilitates the hydrogen abstraction during the grafting reaction. Later it was found that the acid modified the partition coefficient of the styrene between the polymer film and the external liquid phase leading to an increase in the local styrene concentration around the growing chains (Garnett et al., 1979; Ang et al, 1983; and El-Assy, 1991). Subsequently, the degree of grafting is enhanced.

4.5 Effect of Inhibitor

Table 4.1 shows the effect of Mohr's salt (0.1 wt %) on the degree of grafting of styrene onto LDPE. The results demonstrate that the addition of Mohr's salt considerably enhanced the degree of grafting at various styrene concentrations. This can be reasonably attributed to the suppression of the interaction between styrene molecules and their radicals in the grafting mixture and hence the inhibition of homopolymerization. This effect reduces the viscosity and enhances the diffusibility of the styrene into the core of the polymer resin and consequently the degree of grafting increases.

Table 4.1: Effect of Mohr's salt on the degree of grafting (%) of styrene (60 vol. %) onto LDPE at irradiation dose of 20 kGy.

Styrene concentration Vol. %	Degree of grafting (%)	
	without Mohr's salt	0.1 wt % Mohr's salt
20	1.5	5.2
40	5.1	15.3
60	26.6	36.7
80	32.9	50.8
100	23.5	35.2

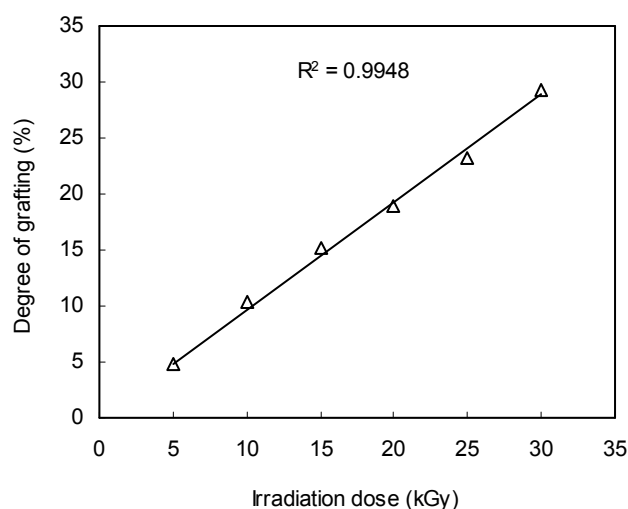


Figure 4.4: The degree of grafting vs. irradiation dose for grafting of styrene having a concentration of 60 vol% in dichloromethane onto LDPE at a dose rate of 0.37 Gy/s.

4.6 Effect of Irradiation Dose

Figure 4.4 shows the relationship between the degree of grafting and irradiation dose for grafting of styrene having a concentration of 60 vol% in dichloromethane onto LDPE resins at a dose rate of 0.37 Gy/s. As can be seen, the degree of grafting increases linearly with the increase in irradiation dose from 5 to 30 kGy. This is due to the fact that higher irradiation doses lead to the formation of more free radical in the grafting mixture; consequently more radicals are available for grafting reaction. Furthermore, the linear relationship indicates that the degree of grafting depends on the amount of radicals formed in the grafting mixture.

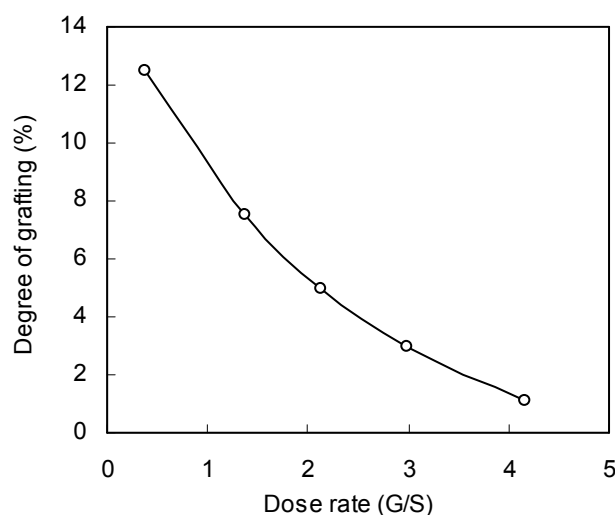


Figure 4.5: The dose rate vs. the degree of grafting of styrene onto LDPE resins.

4.7 Effect of Dose Rate

Figure 4.5 displays the effect of dose rate ranging from 0.37 to 4.17 Gy/s on the degree of grafting of styrene onto LDPE resins. It can be obviously seen that the degree of grafting has an inverse relation with the dose rate i.e. low degree of grafting is obtained at high dose rate and vice versa. At high dose rate, the formed radicals tend to decay by recombination resulting in high chance for homopolymerization which cause considerable increase in the viscosity of the grafting mixture. Consequently, a significant hindrance in styrene diffusibility to the internal grafting layers and fast termination of polystyrene growing takes place. Therefore, the degree of grafting decreases. In contrast, irradiation at low dose rate allows an adequate time for radicals to survive and reacts with monomer molecules and therefore reduces the chance for homopolymerization. As a result, the diffusibility of the monomer to the internal layers is enhanced. Hence, an increase in polystyrene growing chains and in the overall degree of grafting takes place. The above results suggest low radiation dose rates are favorable in irradiation of polymer resins particularly in simultaneous irradiation where homopolymerization is most likely encountered. This effect was properly discussed by Chapiro (1959) with

particular reference to grafting onto PTFE where this effect is severe and by El-Assy (1991) with particular reference to enhancement of grafting of styrene onto polyethylene (PE) by acid addition.

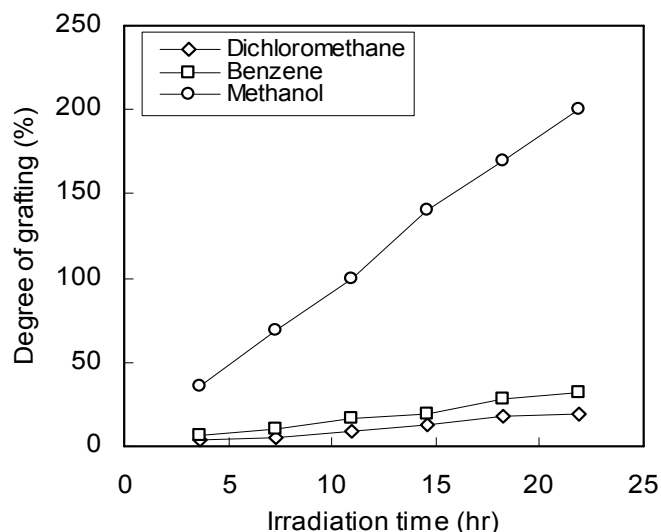


Figure 4.6: The degree of grafting of styrene diluted with various solvents onto LDPE vs. irradiation time.

4.8 Effect of Solvent

The effect of the type of solvent on radiation grafting of styrene onto LDPE films is shown in Figure 4.6. As can be clearly seen from the figure, the dilution of styrene with methanol greatly enhanced the degree of grafting as compared to the dilution with benzene and dichloromethane. The enhancement of grafting by methanol is owing to Thromsdorff effect. These results are consistent with those obtained by Machi et al (1970) and Omichi and Araki (1976). They observed that the degree of grafting of styrene onto PE film was changed by varying solvent and solvent/monomer composition and reached its maximum value when the content of methanol in styrene/methanol mixture was 70 %.

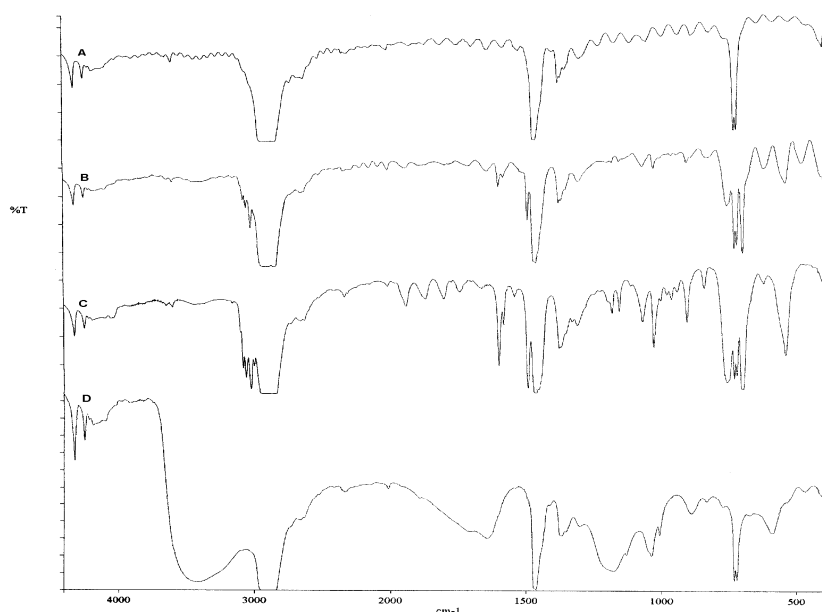


Figure 4.7: FTIR spectra of (A) original LDPE particles; (B) 12 % grafted LDPE-g-PS; (C) 60 % grafted LDPE-g-PS and (C) 60 % grafted LDPE-g-PSSA resins.

4.9 Characterization of the Grafted Resins

4.9.1 Evidence of Grafting

Grafting of polystyrene onto LDPE particles and its subsequent sulfonation were confirmed by FTIR spectral analysis. Typical FTIR spectra of the resin (60 % degree of grafting) and its corresponding grafted and original LDPE resins are shown in Figure 4.7. Compared to original LDPE particles (A), the spectrum of the polystyrene grafted LDPE (PE-g-PS) resins (C), contains additional peaks representing benzene ring features at 3050 cm^{-1} , 1500 cm^{-1} and 1600 cm^{-1} , respectively. The presence of aromatic out-of-plane C-H deformation band at 860 cm^{-1} and C- H bending overtone and combination bands in the region of $1660\text{--}2000\text{ cm}^{-1}$ is due to mono-substitution of benzene ring. The size of the characteristic peaks of benzene ring increases with the increase in the degree of grafting as clearly seen from the spectra of 7 % of LDPE-g-PS resin (B) when compared to that of 60 % one

(C). The sulfonated resin (LDPE-g-PSSA) (D) was characterized by the emergence of three new sharp bands at 1126, 1034 and 1007 cm^{-1} representing SO_3^- groups. The broad band at 3200-3600 is due to the -OH groups of water molecules strongly bound to SO_3^- groups by hydrogen bonding. These results confirm that grafting and subsequent sulfonation permanently modified the chemical structure of the LDPE matrix by introducing sulfonated polystyrene grafts and the final membranes have a strong hydrophilic nature.

4.9.2 Structural Changes

X-ray diffractometry measurements were carried out in this study to investigate the structural changes owing to the introduction of polystyrene grafts to the LDPE particles.

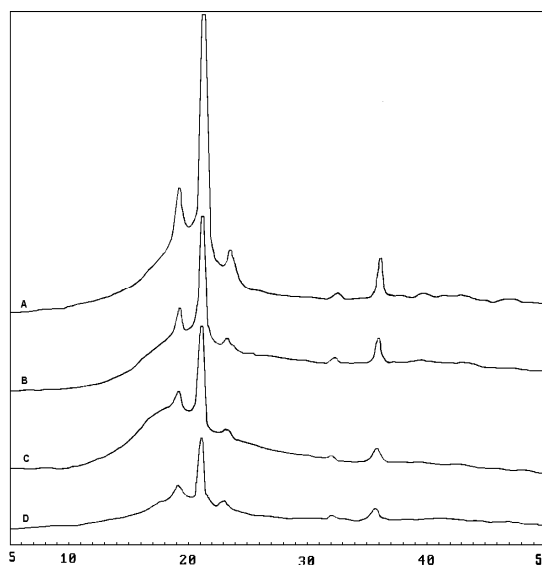


Figure 4.8: XRD diffractograms of LDPE-g-PS resins having various degrees of grafting: (A) 24 %; (C) 42 % and (D) 60 %.

Diffraction patterns of the original and grafted LDPE having various degrees of grafting are shown in Figure 4.8. It can be obviously seen that a remarkable decrease in the degree of crystallinity takes place as a result of grafting and the amount of such decrease depends mainly on the degree of grafting. Higher degrees of grafting lead to lower degrees of crystallinity and vice versa as illustrated from the inverse proportional relationship between the peak intensity and the degree of grafting. The effect of grafting on the crystallinity for all grafted resins shows slight shift in the angle (2θ) compared to the original resin which may reflect certain changes in the chemical structure. These results suggest that the reduction in the crystallinity of the grafted resins is due to the dilution of the structure with the amorphous polystyrene grafts to LDPE.

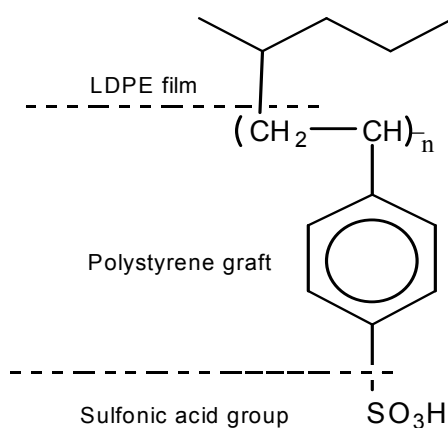


Figure 4.9: Generalized molecular structure of LDPE-g-PSSA resins.

4.10 Properties of Sulfonated Resins

A generalized molecular structure of the LDPE-g-PSSA resins is given in Figure 4.9. A degree of sulfonation of 100 % was achieved in all membranes and thus the membrane properties were only presented and discussed in correlation with the degree of grafting.

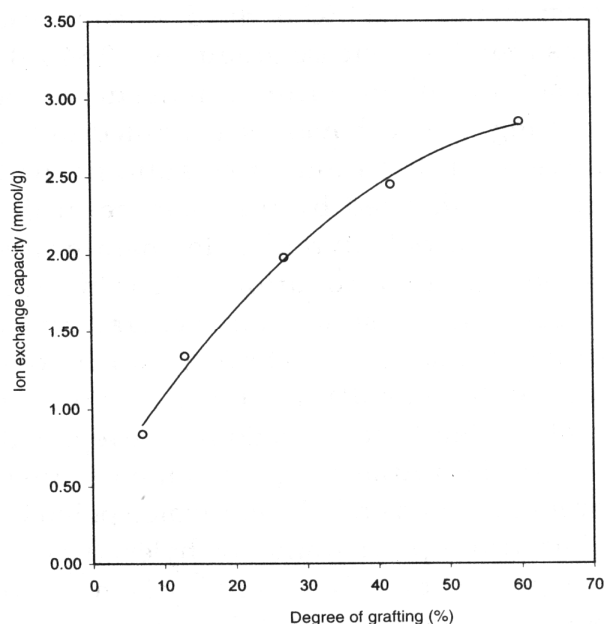


Figure 4.10: Relationship between the ion exchange capacity (IEC) and the degree of grafting of LDPE-g-PSSA resins.

4.10.1 Ion Exchange Capacity

Figure 4.10 shows the relationship between the ion exchange capacity (IEC) and the degree of grafting of LDPE-g-PSSA resins. The IEC of the dry membrane was found to increase gradually (0.84-2.85 mmol/g) with the increase in the degree of grafting. This behavior is attributed to the increase in the number of sulfonic acid groups enhanced by the increase in the number of polystyrene side chain grafts subjected to sulfonation. These results suggest that desirable ionic characters in cation exchange membranes can be obtained by variation of the degree of grafting.

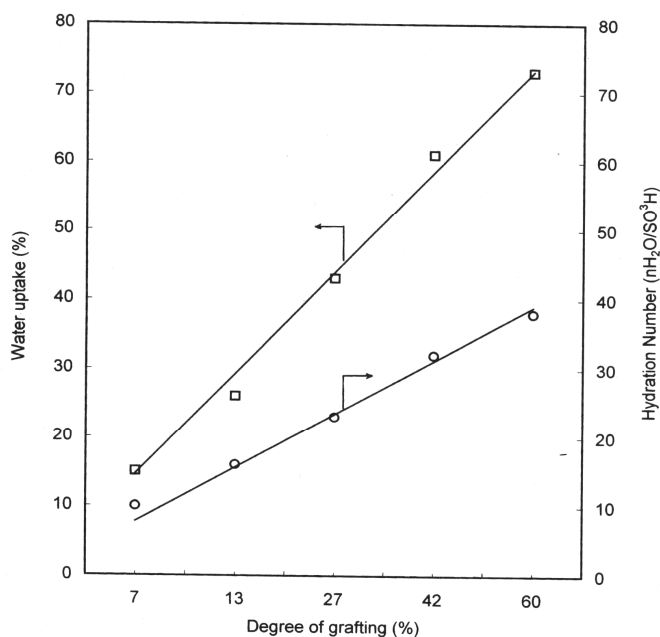


Figure 4.11: Relationship between water uptake coupled with hydration number and the degree of grafting of LDPE-g-PSSA resins.

4.10.2 Swelling Behavior

Swelling of LDPE-g-PSSA resins having various degrees of grafting in deionized water was investigated in terms of water uptake and hydration number i.e. number of water molecules per sulfonic acid groups ($\text{nH}_2\text{O}/\text{SO}_3\text{H}$). The variation of the membrane water uptake and the hydration number with the degree of grafting of LDPE-g-PSSA resin is shown in Figure 4.11. Both water uptake and hydration number were found to increase gradually with the increase in the degree of grafting. The former increase is due to the increase in the hydrophilicity imparted to the membranes as a result of incorporation of more hydrophilic sulfonic acid groups. The latter increase is ascribed to the cumulative effect of three main factors: the increase of hydrophilicity, the decrease in the hydrophobicity and the structural changes taking place during the resins preparation procedure (grafting and sulfonation).

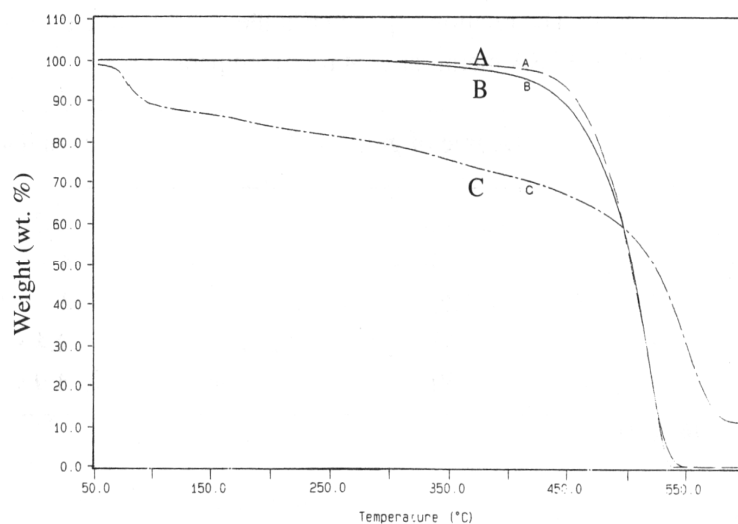


Figure 4.12: TGA thermograms of: (A) original LDPE; (B) 42 % grafted LDPE-g-PS and (C) 42 % grafted PE-g-PSSA resins.

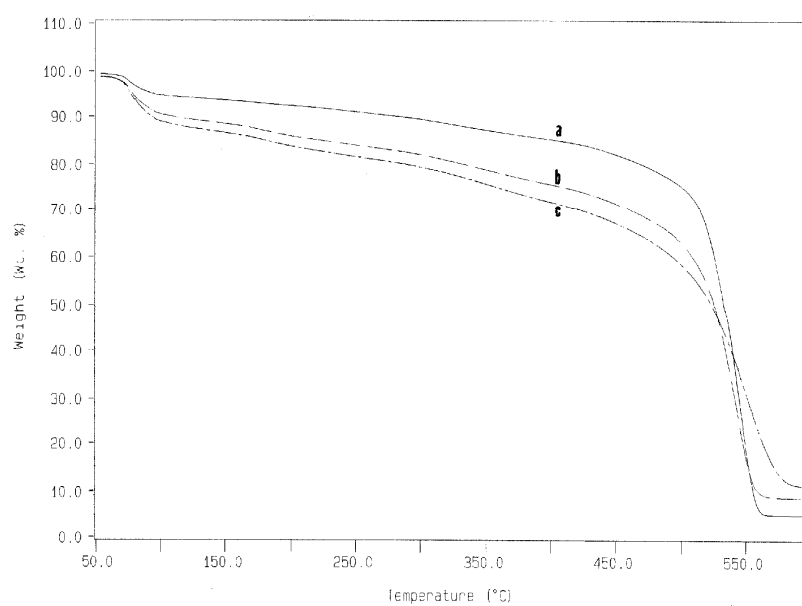


Figure 4.13: TGA thermograms of LDPE-g-PSSA resins having various degrees of grafting: (A) 24 %; (C) 42 % and (D) 60 %.

4.10.3 Thermal Stability of Grafted and Sulfonated Resins

TGA thermograms of original LDPE and 42% grafted LDPE as well as LDPE-g-PSSA resins having the same degree of grafting are presented Figure 4.12. Original and grafted LDPE resin were analyzed to investigate the effect of the membrane preparation procedure (grafting and sulfonation) on the thermal stability on the starting LDPE matrix. As can be seen from thermogram 'A', the original LDPE film is stable up to approximately 320°C. This is followed by one-step degradation pattern.

Grafting of styrene onto LDPE resins resulted in a polystyrene grafted resins also having one-step decomposition pattern under the influence of heat treatment. Both of the incorporated polystyrene grafts and the LDPE matrix undergo non-distinct degradation temperature starting at 370 °C as depicted from thermogram 'B'. It is found that the presence of polystyrene grafts in the grafted film brings an increase to the inherent decomposition temperature of the LDPE matrix. These results suggest that polystyrene side chain grafts are highly compatible with LDPE matrix and they form one phase microdomains in the grafted resins. Such compatibility is a result of the similarity in the nature of the hydrocarbon structure of both of the grafted resin components.

Sulfonation of the grafted resins introduces three-step degradation patterns as depicted from thermogram 'C'. In the first step, the weight lost starts below 100 °C and continued up to ~160 °C. This followed by another two degradation steps at ~200 °C and 430 °C, respectively. The weight loss starts at 50 °C and continues up to 160 °C is due to the removal of water bound to the hydrophylic sulfonic acid groups present in the membrane during the initial heating. The remaining of some water up to temperatures higher than 100 °C is due to the strong hydrogen bonding between some water molecules and sulfonic acid groups.

The massive degradation of the LDPE-g-PSSA resins taking place at a temperature of 200 °C is attributed to the removal of the sulfonic acid groups. The final degradation pattern at the temperature of 430 °C is due the decomposition of LDPE matrix. These results indicate that the incorporation of sulfonic acid groups

improves the stability of LDPE matrix. However, the degradation region represented by the continuous weight loss observed in the thermogram in the range of 200-420 °C does not show clear discrimination between the temperatures of the removal of the sulfonic acid groups (desulfonation) and the decomposition of polystyrene grafts. These observations suggest that the sulfonation of polystyrene grafted LDPE make the resins more susceptible to thermal decomposition than original and only grafted resins. Based on the aforementioned results, it may be stated that the membranes are thermally stable up to ~200 °C under the present experimental conditions.

The TGA thermograms of LDPE-g-polystyrene sulfonic acid resins having various degrees of grafting are presented in Figure 4.13. All the membranes show three-step degradation patterns due to dehydration, desulfonation, and LDPE matrix degradation. However, membranes having degree of grafting as high as 60 % were found to show one additional degradation step at 370°C due to decomposition of polystyrene grafts. It is also found the membranes do not undergo complete degradation and some of the residues are left behind at the end of thermograms in contrast to the original and grafted resins (non-sulfonated). Such behaviour suggests that sulfonic acid groups play an important role during the degradation of the membranes in such a way that enhances stability of the LDPE matrix and the residue formation.

It can be seen that the decomposition temperature of LDPE matrix (340°C), decomposition temperature of the polystyrene grafts (370°C) and the desulfonation temperature (200°C) were found to remain unchangeable for all the membrane regardless the content of sulfonated polystyrene grafts. These results suggest that the desulfonation is independent process and do not interfere with the degradation of LDPE matrix in all membranes. The interesting behaviour that can be observed in the thermograms is that the membranes do not undergo complete degradation in contrast to the original as well as grafted resins. Instead, some of the residues are left behind at the end of the heating run. It can be seen that the residual weight increases with the increase in the degree of grafting i.e. the amount of sulfonated polystyrene grafts. Such behaviour indicates that the sulfonic acid groups play a significant role during the degradation of the membranes in such way that it enhances the ash formation from the LDPE matrix.

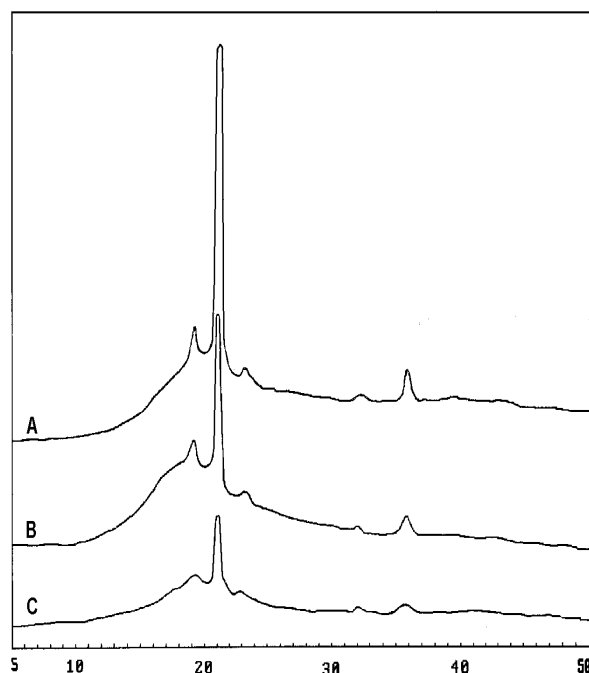


Figure 4.14: X-ray diffractograms of: (A) original LDPE, (B) 60 % grafted LDPE-g-PS and (C) 60 % grafted LDPE-g-PSSA resins.

4.10.4 Structural Changes in Grafted and Sulfonated Resins

To have a preliminary idea on the structural changes took place in the LDPE resin upon grafting and subsequent sulfonation, XRD qualitative analysis was conducted on LDPE-g-PS resins and LDPE-g-PSSA resins both of which possess the same degree of grafting. Original LDPE resin is used as a reference. Figure 4.14 shows typical x-ray diffraction patterns of original PE resin and 60 % grafted LDPE-g-PS resin and its counterpart LDPE-g-PSSA resin. The diffractogram of the original LDPE resins (A) shows a typical morphology of semicrystalline polymer where two regions representing the crystalline (strong peaks) and the amorphous (flat peaks) fractions, can be recognized. Grafting is found to reduce the degree of crystallinity and so does the sulfonation as indicated by the reduction of the relevant crystallinity peak size shown in diffractograms B and C, respectively. However, the diffraction angle (2θ) records no remarkable shift indicating the absence of any significant changes in the crystalline structure of the PE resins and no new phase

formed during grafting and subsequent sulfonation. These results suggest that both grafting and sulfonation affected the crystalline structure of the LDPE resins by a dilution effect and polystyrene grafting took place in the entire amorphous region without penetrating the crystallites.

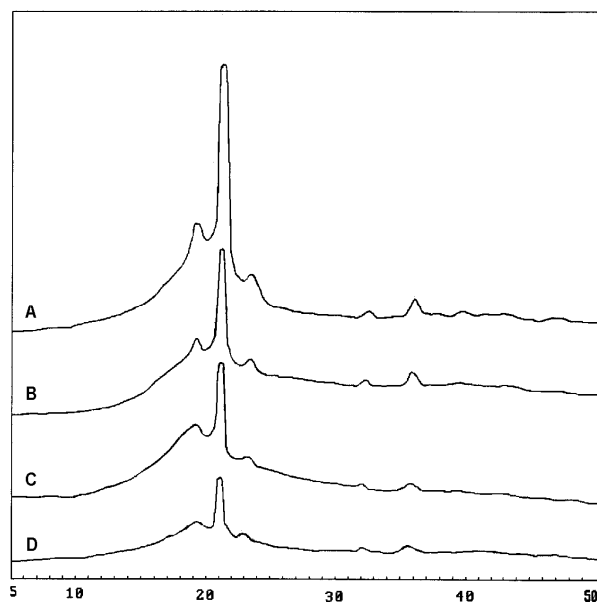


Figure 4.15: X-ray diffractograms of LDPE-g-PSSA resins having various degrees of grafting: (A) 7 %; (B) 24 %; (C) 42 % and (D) 60 %.

To further elucidate the effect of variation of the degree of grafting on the crystallinity of the membranes, XRD measurements were also conducted on membrane samples having various degree of grafting. Figure 4.15 shows typical x-ray diffractograms of LDPE-g-PSSA resins having various degrees of grafting. It is obvious that the peak intensity decreases with the increase in the degree of grafting indicating that the reduction in the degree of crystallinity is a function of the degree of grafting. Also, there is no remarkable shift in Bragg's angle (2θ). These results indicate that the reduction in the crystallinity of the membranes is mainly due to the dilution of the crystalline structure with the amorphous polystyrene grafts, which increase gradually with the degree of grafting. Nevertheless, XRD qualitative analysis alone does not provide any decisive information on the structural changes took place in the membranes prepared in this work. Thus, further exploration on the nature of the structural changes in the membranes and quantitative analyses including crystallinity calculations are sought. Calculation of the degree of crystallinity in the

polymer is important since crystallinity affects most of the physical properties. To achieve this, DSC measurements were conducted on samples similar to those used for XRD measurements and the analysis included the determination of the thermal properties i.e. melting temperature and heat of melting in correlation with preparation procedure and the variation of the degree of grafting.

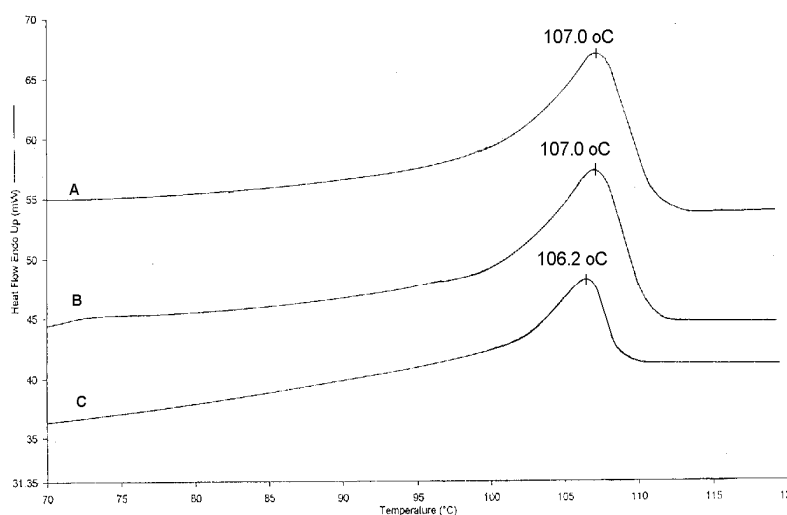


Figure 4.16: DSC thermograms of: (A) original PE; (B) 60 % grafted LDPE-g-PS and (C) 60 % grafted LDPE-g-PSSA resins.

4.10.5 Changes in Thermal Properties of Grafted and Sulfonated Resins

Figure 4.16 shows DSC thermograms of the original (pre-grafted) LDPE and 60 % PE-g-PS and 60 % grafted LDPE-g-PSSA resins. As can be seen, the original LDPE particles show a single melting endothermal peak at 107.0 °C. The shape of this peak remains unchanged after grafting and subsequent sulfonation despite the reduction in its area, which seems to be highly considerable upon sulfonation as depicted in Figure 6 (A-C). Moreover, the melting temperature (T_m) of LDPE-g-PS resins was not affected by grafting and remained at 107.0 °C unlike that of LDPE-g-PSSA resins, which was marginally decreased to 106.2 °C. In addition, the heat of melting (ΔH_m) obtained from the area under the melting peaks and the calculated

degree of crystallinity obtained from equation 2 were reduced by grafting and the subsequent sulfonation. For instance, ΔH_m was reduced from 63.2 to 32.8 J/g by grafting (60 % polystyrene) and to 6.1 J/g by sulfonation whereas, the degree of crystallinity of the same samples decreased from 21.8 to 11.3 and 2.3, by grafting and the followed sulfonation, respectively.

The decrease in the ΔH_m and the degree of crystallinity by grafting can be explained based on the fact that grafting reaction was carried out at room temperature (28°C), which is far below the T_m of LDPE resins that has a very low swelling tendency hindering the diffusion of most of the monomers at room temperature. Consequently, it can be suggested that styrene diffuses only through the amorphous part of the PE matrix causing no swelling to the crystallites and forms polystyrene grafts in the entire amorphous region and at the surface of the crystallites despite the presence of the radicals in both crystalline and amorphous regions. This leads to a remarkable increase in the amorphous content, which exerts a dilution effect on the crystalline structure of the resins without any significant disruption in the inherent crystallites of LDPE matrix. This explanation is supported by the absence of any variation in the T_m upon grafting indicating the original crystal size distribution in PE resin has not been affected. It is also in accordance with the fact that grafting of styrene diluted with 1,2-dichloromethane in the present system is a diffusion-controlled process whereby grafting proceeds by front mechanism (Nasef and Hegazy, 2004).

The reduction in the ΔH_m and the degree of crystallinity with sulfonation, which was accompanied by a marginal reduction in the T_m , reflects the existence of not only an additional dilution effect but also a partial disruption in the crystallites of the LDPE matrix. The additional dilution is believed to be due to the increase in the amorphous fraction by the incorporation of sulfonic acid groups. The partial disruption may be attributed to the penetration of the crystallites by some grafts under the influence of the aggressiveness of sulfonation process and the hydrophilic/hydrophobic stress at grafts-lamellae interface. The latter is a result of the strongly hydrophilic nature of sulfonic acid groups, which prompts it where grafts are attached to the surface of the lamellae causing some of polystyrene grafts

to split-of and partial disruption occurs in the crystallites when the membrane swells. It can be concluded that the cumulative effect of the dilution of the crystalline structure with the amorphous polystyrene and the crystal partial disruption caused by the possible penetration of some grafts during sulfonation and the rupture in the crystallites during the hydration are accounted for the changes in the heat of melting and the degree of crystallinity of the LDPE-g-PSSA resins.

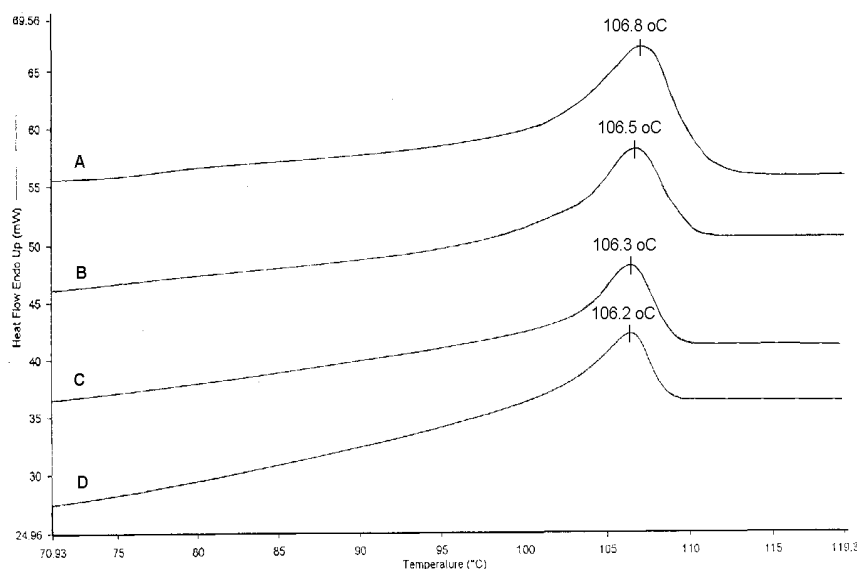


Figure 4.17: DSC thermograms of LDPE-g-PSSA resins having degrees of grafting of (A) 7 %; (B) 24 %; (C) 42 % and (D) 60 %.

To discriminate the role of the dilution effect from that of the crystal disruption during the structural changes taking place upon grafting and sulfonation, DSC measurements were conducted on sulfonated resins with various degrees of grafting. Figure 4.17, show typical DSC thermograms of LDPE-g-PSSA resins having various degrees of grafting. The melting endotherms of all LDPE-g-PSSA resins show peaks of similar shape despite the differences in the beginning of each peak with the area under them steeply decreasing in an inverse relationship with the degree of grafting. This was coupled by a tiny down shift in the T_m of the membranes with the increase in the degree of grafting. This decreasing trend can be clearly seen in Figure 4.18 in which T_m of the sulfonated resins was plotted against the degree of grafting. The straight line is representing the T_m of LDPE-g-PS resins.

The slight reduction in T_m with the increase in the degree of grafting is responsible for some disorder in the crystalline structure (reduction in the crystal size) mostly arising from the the disruption in the crystallites by the incorporation of sulfonic acid groups in the membranes. The reduction in the crystal size increases with the increase in the degree of grafting due to introducing of more sulfonic acid groups.

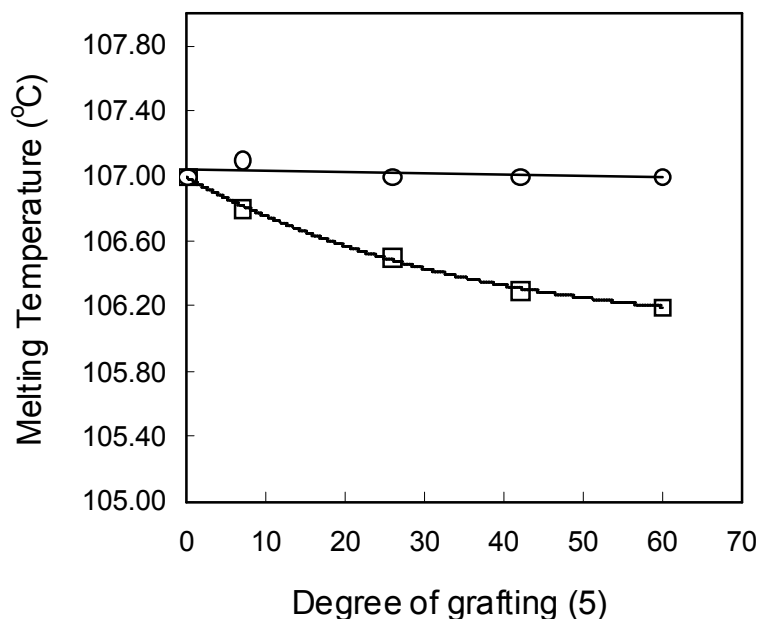


Figure 4.18: The relationship between the melting temperature (T_m) and the degree of grafting for (O) LDPE-g-PS and (\square) LDPE-g-PSSA resins.

The changes in the peak areas of both grafted and final resins were also reflected in a form of a continuous decrease in the ΔH_m with the increase in the degree of grafting as depicted from correlations presented in Figure 4.19. However, the decreasing trend of ΔH_m in the grafted resin is linear and that in sulfonated resin is non-linear. The former confirms that the incorporated polystyrene exerts only dilution effect on the crystalline structure of LDPE at all grafting levels and the variation in the heat of melting is a function of the fraction of PE matrix in the grafted resins. Whereas, the latter confirms that the dilution effect is not the only factor affecting the crystalline structure but also, the partial disruption taking place in the crystallites as a result of introducing sulfonic acid groups, which increases with the increase in the sulfonic acid content. It can be stated that both dilution and partial

disruption affect the heat of melting of the membranes simultaneously but in an independent manner.

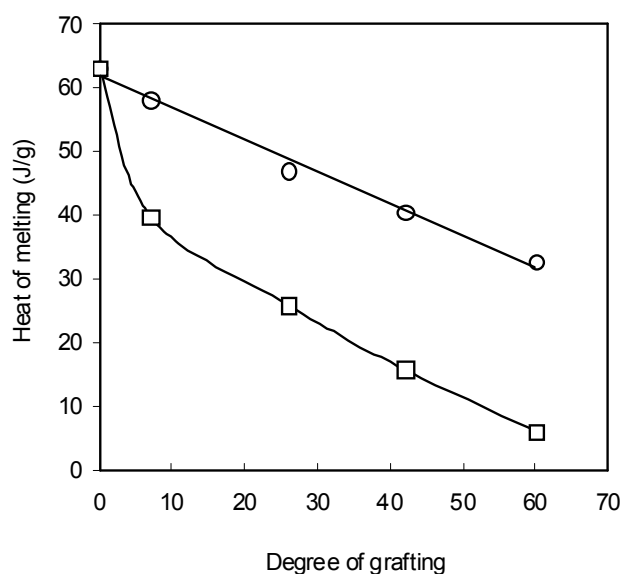


Figure 4.19: The variation of the heat of melting (ΔH_m) with the degree of s. grafting for (O) LDPE-g-PS resins and (□) LDPE-g-PSSA resins.

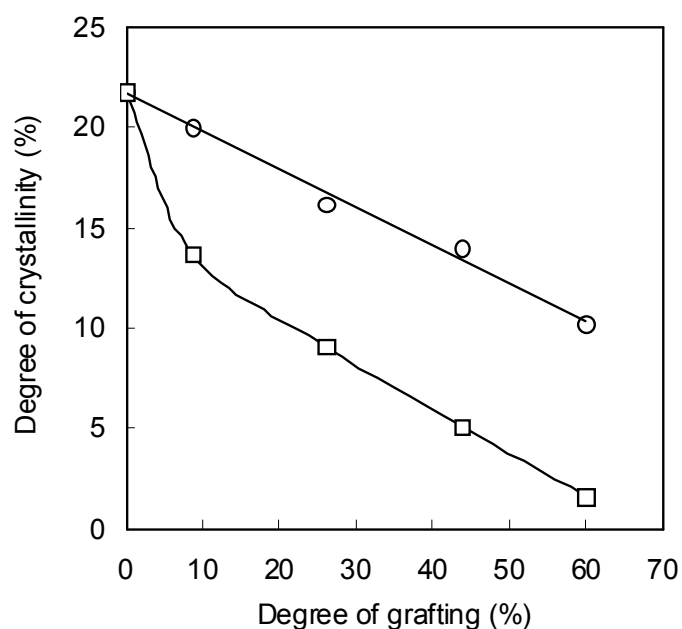


Figure 4.20: The variation of the degree of crystallinity with the degree of grafting for (O) LDPE-g-PS resins and (□) LDPE-g-PSSA resins.

The variation in the degree of crystallinity of the membranes with the degree of grafting compared to that of the grafted films is shown in Fig 4.20. All the grafted and the sulfonated resins show continuous decrease in the degree of crystallinity, which is linear in PE-g-PS and non-linear in LDPE-g-PSSA resins. This behavior is on line with the recorded variation in the ΔH_m and can be attributed to the dilution effect in case of LDPE-g-PS and to the cumulative effect of the dilution and the partial disruption in the inherent crystallinity of LDPE-g-PSSA resins. The conclusion that can be drawn is that despite the changes in the structural and thermal properties of LDPE-g-PSSA resins with the variation of the content of polystyrene sulfonic acid, their crystallinity remains confined to the LDPE fraction. The results DSC analysis explained the part of the structural behavior that could not be seen by XRD qualitative analysis in which the intensity of the crystalline reflection peaks were found to decrease with the increase in the degree of grafting and was only attributed to dilution effect.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Cation exchange resins containing sulfonic acid functionality were successfully prepared radiation induced grafting method. The resins were prepared using simultaneous irradiation grafting of styrene monomer onto LDPE particles under various grafting conditions. The grafted resins were subsequently sulfonated using chlorosulfonic acid/dichloromethane mixture under controlled conditions. Various properties of the obtained grafted and sulfonated resins were investigated using analytical and materials research aspects. Based the present study the following conclusion can be made:

1. The degree of grafting was found to be strongly dependent on the grafting conditions namely monomer concentration, irradiation dose, dose rate, solvent and addition of Mohr's salt as well as sulfuric acid. These conditions were found to affect two the phenomena controlling the grafting process i.e. the ability of the monomer to diffuse through the grafted layer, and the concentration of the radical in the surface of the resin.
2. The structural changes of the grafted LDPE resins were found to depend on the degree of grafting. Therefore suitable degree of grafting as well as properties can be achieved in the grafted film via proper selection of the grafting conditions.
3. Investigation of the properties (ion exchange capacity, swelling behavior, ionic conductivity and thermal as well as mechanical stability) of LDPE-g-PSSA resins prepared by radiation-induced grafting of styrene onto LDPE followed by sulfonation revealed that the resins properties such as water uptake, hydration number and ion exchange capacity were found to be strongly dependent upon the degree of grafting.

4. The LDPE-g-PSSA resins was found to be thermally stable up to around 200°C beyond that it degrades in a two-step degradation pattern due to the elimination of sulfonic acid groups and the decomposition of the LDPE matrix.
5. The LDPE-g-PSSA resins found to undergo structural changes under the effect of preparation procedure. Grafting was found to impose a dilution effect on the crystallinity by incorporating amorphous polystyrene entirely in noncrystalline region of LDPE matrix without causing any disruption in the crystalline structure as indicated by the absence of changes in T_m at all grafting levels. Sulfonation induces a combined dilution and partial disruption effects to the inherent crystallinity of LDPE resins under the influence of crystalline penetration by some grafts and hydrophilic/hydrophobic stress at grafts-lamellae interface, which ruptures the crystallites upon hydration. The increase in the degree of grafting increases the content of sulfonic acid groups and consequently the degree of crystallinity decreases. The crystalline fraction in PE resin represents the overall crystallinity of these membranes.

5.2 Recommendations

1. Graft copolymerisation of styrene in this study was carried out by simultaneous irradiation technique, which was found to be convenient at low irradiation doses and dose rates. It is recommended to try to adapt other irradiation techniques, which utilize higher irradiation doses and dose rates such as preirradiation in air to enhance the preparation of the membrane at large scale.
2. The cation exchange resins prepared in this study were found to have a strong hygroscopic nature and their water uptake depends upon the amount of incorporated sulfonic acid groups. Moreover, the thermal investigation of the membranes showed that the water absorbed is strongly bound to the membranes as its release continued to temperatures above 100°C. It is recommended that a study on the states of water and water sorption characteristics to be made. Besides, the correlation between the structural changes and the variation of water fractions in the membranes should be studied.

3. The obtained cation exchange resins seem to have very good combination of physical and chemical properties. It is highly recommended to test them for removal of heavy metal ion from aqueous solutions under various reaction parameters such as initial metal ion concentration, pH of the adsorption medium and temperature and establish their adsorption equilibrium and kinetics.
4. It is highly recommended to test them for removal of dyes from aqueous solutions under various reaction parameters such as initial metal ion concentration, pH of the adsorption medium and temperature and establish their adsorption equilibrium and kinetics.
5. It is also highly recommended to adopt radiation induced grafting method to graft other monomers that bring other functional groups existing polymer substrate for the purpose of developing cheap resins for waste water treatment.

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